Helicate self-assembly from heterotopic ligand strands of specific binding site sequence

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Linear ligands containing a sequence of three bipyridine B and terpyridine T units form homo- or hetero-nuclear duplex helicates with Cu^I, Cu^{II} and Fe^{II} ions; of particular interest is the case of a $[(BTB)Cu^{II}Cu^{II}Cu^{II}(TBT)]$ combination which amounts to the translation of one strand into the other one by virtue of the B–T correspondence established by the five-coordinate Cu^{II} ions.

The spontaneous self-assembly of inorganic architectures from suitably designed organic ligands and specific metal ions is directed by the steric information stored in the ligands and the coordination algorithm of the metal ion.[1] Linear sequences of discrete metal-ion binding sites may serve as molecular strands containing information that may be read out and processed by metal-ion complexation.

In particular, sequential ligand strands containing repeating bidentate units such as 2,2′-bipyridine (B), separated into discrete sites by a suitable spacer, combine with metal of tetrahedral coordination geometry (*e.g.* Cu^I, Ag^I) to produce homostrand double-helical metal complexes, duplex helicates.[1–5] Similarly, a strand of tridentate 2,2′ : 6′,2″-terpyridine sites (T) yields duplex helicates with octahedral metal ions such as Fe^{II}.[2,6,7] Finally, heteroduplex helicates are assembled from BBB and TTT strands by means of the five-coordinate Cu^{II} ion.[8]

These self-assembly processes result from reading the molecular information stored in the binding subunits by a specific metal ion, following a given coordination algorithm.

A similar reading process occurs in the formation of the DNA double helix which assembles *via* the complementary hydrogen-bonding patterns of the base pairs of two mixed polynucleotide strands. The nucleotide components and the base pairing by hydrogen bonding find their correspondence in the ligand binding sites and the metal-ion coordination respectively. In addition, whereas base pairing in nucleic acids is restricted to a planar geometry the metal ions offer a variety of coordination geometries which may bring together binding subunits in different orientations depending on the subunit/metal-ion couple, thus enriching greatly the capabilities of inorganic systems to process chemical information.

An important further step is to design linear ligands containing a given sequence of binding subunits and to study their self-assembly into heterosite homo- or hetero-duplex complexes with identical or different metal ions (homo- or hetero-metallic). We illustrate here our work along these lines by presenting some of the results obtained with the mixed-site strands BTB, TBT and BBT and Cu^I, Cu^{II} or Fe^{II} metal ions.

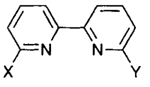
The functionalized B and T subunits **2**–**4**, **6**–**8** were obtained from the parent compounds **1**, **5** and **6**.[9] Condensation of 2 equiv. of **2** with 1 equiv. of **8** ($KOBu^t$, thf, reflux, 21 h) gave BTB (mp 202–204 °C, 54%). The other ligands were obtained in a similar fashion: TBT (mp 196–198 °C) from 1 equiv. of **4** and 2 equiv. of **7** (reaction time 3 h, 55%); BBT (mp 206–208 °C) from 1 equiv. of **2** and 1 equiv. of **3** to give a monobromomethyl dimeric compound (3 h, mp 142 °C, 35%) which was reacted with 1 equiv. of **9** (1.5 h, 60%).

Complexation studies were performed in similar conditions [MeCN–$CHCl_3$ (1 : 1); room temp., 2–3 h] using different combinations of two ligands and a given set of metal salts, $[Cu(MeCN)_4]BF_4$, $[Cu(H_2O)_6][BF_4]_2$ or $Cu[CF_3SO_3]_2$, and $[Fe(H_2O)_6][BF_4]_2$. Addition of the required amounts of the salts to a suspension of the ligands led to dissolution and formation of a distinctive colour. Slow evaporation of diethyl ether into the solution induced precipitation of the complexes which were isolated and characterized by electrospray mass spectrometry (ESMS) and ^1H NMR as well as microanalysis when feasible.

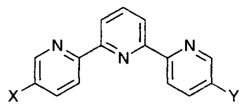
The ligand BTB (2 equiv.) binds Cu^I (2 equiv.) and Fe^{II} (1 equiv.) in MeCN to give a complex of composition $[FeCu_2(BTB)_2][BF_4]_4$ as determined by ESMS where the M^{4+}, M^{3+} and M^{2+} ions are detected. The reaction occurs readily at room temp. when Fe^{II} is added before Cu^I; when Cu^I is added first heating is required to form the complex, presumably due to competition of Cu^I at the tridentate terpy sites. Examination of the differences between the ^1H NMR spectra of the ligand and that of the complex, as well as comparison with the spectra of the known helicates of related tris-B[3] and tris-T[7] ligands with $3Cu^I$ and $3Fe^{II}$ respectively, leads to the conclusion that the complex formed by BTB is a homostranded double helicate of heterotrinuclear type $\mathbf{H_1}$ (Fig. 1) where the Fe^{II} centre is pseudo-octahedrally coordinated by the two tridentate binding units and each Cu^I ion is pseudo-tetrahedrally bound to two bidentate units.

An analogous complex $[Fe_2Cu(TBT)_2][BF_4]_5$ may be envisaged for the TBT ligand. However, owing to the strong binding of Fe^{II} in the TT octahedral site a monomeric head-to-tail complex $[Fe(TBT)][BF_4]_2$ is formed in preference to the desired helicate which was detected by ESMS apparently as a minor product.

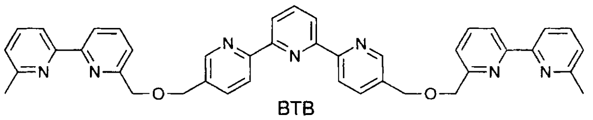
The unsymmetrical ligand BBT may form two homoduplex heterotrinuclear complexes as a result of parallel or antiparallel alignment of the ligands. In the presence of 2 equiv. of Cu^I and 1 equiv. of Fe^{II} the parallel complex $[(BBT)Cu^I$-



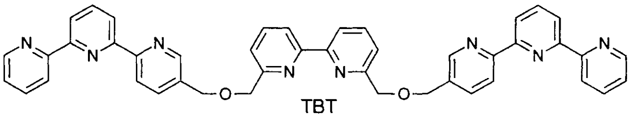
1 X = Y = Me
2 X = Me, Y = CH_2OH
3 X = Y = CH_2Br
4 X = Y = CH_2OH



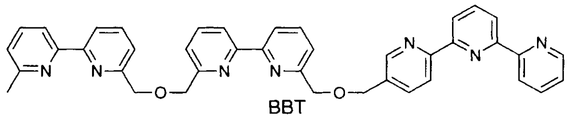
5 X = H, Y = Me
6 X = Y = Me
7 X = H, Y = CH_2Br
8 X = Y = CH_2Br
9 X = H, Y = CH_2OH



BTB



TBT



BBT

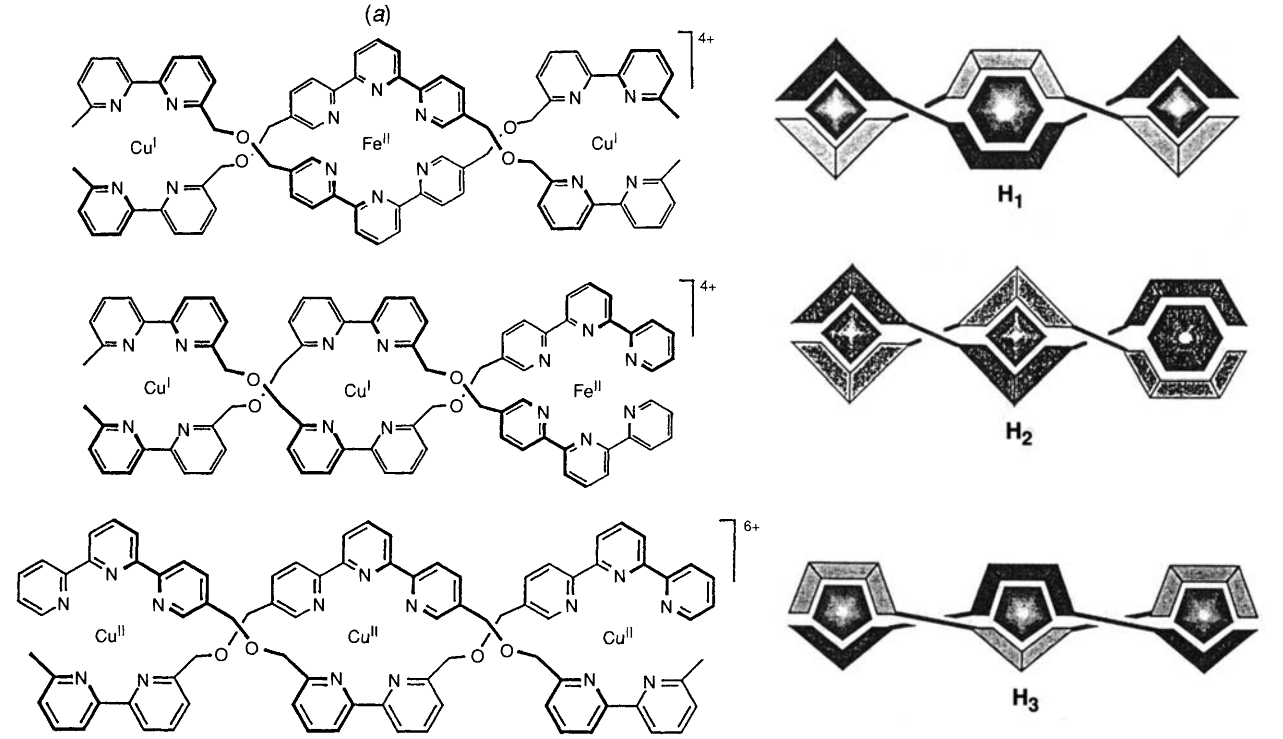


Fig. 1 (*a*) Formulae of the heterotopic helicates $[(BTB)Cu^IFe^{II}Cu^I(BTB)][BF_4]$ $\mathbf{H_1}$, $[(BBT)Cu^ICu^IFe^{II}(BBT)][BF_4]_4$ $\mathbf{H_2}$ and $[(BTB)Cu^{II}Cu^{II}Cu^{II}(BTB)][CF_3SO_3]_6$ $\mathbf{H_3}$, and (*b*) their schematic representation using squares, pentagons and hexagons to designate four-, five- and six-coordinate metal ions respectively

$Cu^IFe^{II}(BBT)]^{4+}$ $\mathbf{H_2}$ self-assembles, whereas with 2 equiv. Cu^{II} and 1 equiv. Cu^I evidence for the formation of the antiparallel complex $[(BBT)Cu^{II}Cu^ICu^{II}(TBB)]$ has been obtained, in line with the $BCu^{II}T$ five-coordination in heteroduplex copper(II) helicates.[8]

The electronic absorption spectra† also correspond to the structures of $\mathbf{H_1}$ and $\mathbf{H_2}$.

With 1 equiv. of each of BTB and TBT and 3 equiv. of Cu^{II} a complex of composition $[Cu_3(BTB)(TBT)][CF_3SO_3]_6$ was obtained as determinated by ESMS identifying the M^{n+} (n = 2–6) ions. By analogy with the formation of a heterostrand trinuclear copper(II) helicate from homotopic tris-B and tris-T ligands,[8] the trinuclear heterotopic and heteroduplex helicate $[(BTB)Cu^{II}Cu^{II}Cu^{II}(TBT)]^{6+}$ $\mathbf{H_3}$ structure may be assigned to the complex.‡

The helicate $\mathbf{H_3}$ is of particular interest since it represents a case of translation of a given sequence of B and T units into the complementary sequence by virtue of the heterotopic B ⟷ T correspondence established by the five-coordinate Cu^{II} ions, which act as translator, whereas Cu^I and Fe^{II} effect duplication (copying) *via* homotopic B ⟷ B and T ⟷ T correspondence respectively. Thus the metal ions determine the pairing; they represent the key selecting the dictionary through which and the language into which the translation takes place.

It is clear that the present and earlier[1–3,7,8] results on helicate formation offer a range of intriguing implications and perspectives such as: (*i*) coding *via* the design of specific codon sequences; (*ii*) metal-ion mediated translation which opens the way to (*iii*) replication by generation of the complementary strand from the constituting subunits as is the case for nucleic acid replication. Of course a number of sites other than B and T may be considered, as well as various other metal ions.§ Such metal-ion directed strand combination in helicate self-assembly also forms a coordination-controlled combinatorial chemistry set. Work along these lines is actively pursued.

Footnotes

† λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) in MeCN: 454 (10000), 551 (7000) for $\mathbf{H_1}$; 456 (9000), 551 (8000) for $\mathbf{H_2}$.

‡ With 1 equiv. of BBT, TBT, Cu^{II}, Cu^I and Fe^{II} a mixture of predominantly two complexes was obtained one of which was identified by ESMS as probably being the heteroduplex with three different metal centres $[(BBT)Cu^{II}Cu^IFe^{II}(TBT)]^{5+}$.

§ One may note that in view of the different and characteristic electronic absorption spectra of the coordination centres, BCu^IB, $TFe^{II}T$ and $BCu^{II}T$, optical reading of the helicates may be envisaged.

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