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Mononuclear–dinuclear helicate interconversion of dibromo{*N*,*N′*-bis[(*S*)-1-2-(pyridyl)ethyl]pyridine-2,6-dicarboxamidate}-copper(II) *via* a deprotonation–protonation process†

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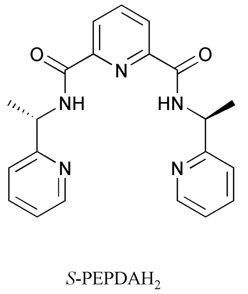
The mononuclear complex dibromo{*N*,*N*’-bis[(*S*)-1-2-(pyridyl)ethyl]pyridine-2,6-dicarboxamidate}copper(II) reversibly converts to the dinuclear chiral (*M*)-helicate upon deprotonation–protonation of the amide ligand; the helicate formation process displays a high level of self-recognition, and equal amounts of the (*P*) and (*M*) helicates only are formed from a racemic mixture of the amide ligand and $\mathbf{CuBr_2}$.

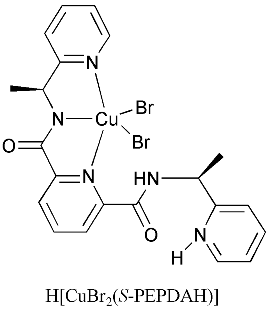
Helicates are an important class of target compounds for supramolecular synthetic chemistry and it is anticipated that in many cases intriguing self-assembly processes will be involved in their formation.[1] If appropriate metal ions are used during the helicate self-assembly process, the information stored in the ligand is recognized and expressed efficiently.[2,3]

Increasing the information that is encoded in a ligand increases the range of possible superamolecular structures that could be produced when this information is read out during helicate formation.[4–6] The presence of one or more chiral centers in a ligand provides the possibility that selective, complementary aggregation of the ligands will occur during homoleptic helicate assembly. In the case of copper(I) with *trans*-cyclohexanediamine, only homochiral ligand is accumulated in a helicate.[7–9] On the other hand, several metal helicates have been formed in concert with deprotonation of pentadentate ligands.[10,11]

In this paper we report (i) the stepwise formation of a dicopper helicate from the ligand *N*,*N′*-bis[*S*-1-(2-pyridyl)-ethyl]pyridine-2,6-dicarboxamide (*S*-PEPDAH$_2$)‡ and $\mathrm{Cu^{II}Br_2}$, (II) a facile interconversion between the mononuclear complex H[$\mathrm{Cu^{II}Br_2}$(*S*-PEPDAH)] and the chiral dicopper helicate (*M*)-[Cu(*S*-PEPDA)]$_2$ which is controlled by the removal or addition of HBr, (iii) precise control of the chirality (*P*/*M*) of the helicate *via* the chirality (*S*/*R*) in a ligand, (iv) a self-recognition process that takes place during helicate formation such that only a racemic mixture of the (*M*) helicate (*M*)-[Cu(*S*-PEPDA)]$_2$ and the (*P*)-helicate (*P*)-[Cu(*R*-PEPDA)]$_2$ are formed from a racemic mixture of the ligand, and (v) the X-ray crystal structure of the monomeric complex H[$\mathrm{Cu^{II}Br_2}$(*S*-PEPDAH)] and the dicopper helicate (*M*)-[Cu(*S*-PEPDA)]$_2$.



S-PEPDAH$_2$



H[CuBr$_2$(*S*-PEPDAH)]

The reaction of *S*-PEPDAH$_2$ with $\mathrm{Cu^{II}Br_2}$ in methanol produces H[$\mathrm{Cu^{II}Br_2}$(*S*-PEPDAH)] [eqn. (1)]. The structure of this complex has been determined by X-ray crystallography.§ The Cu(II) ion is coordinated to the carboxamide ligand through the nitrogen atoms of a terminal pyridine, a deprotonated amide, and the central pyridine. The two auxiliary bromide ligands complete the coordination sphere. The nitrogen atom of the remaining terminal pyridine is protonated and so the overall charge of the complex is neutral. The complex is stable in methanol and does not form a helicate without the addition of bases. When heated under reflux in the presence of triethylamine, the complex forms a double strand helicate quantitatively [eqn. (2)]. The helicate is converted back to the mononuclear form instantaneously by the addition of an equivalent amount of HBr. These changes can be followed in the CD spectra (see below).

$$\mathrm{CuBr_2} + S\text{-}\mathrm{PEPDAH_2} \xrightarrow{\Delta/\mathrm{MeOH}} \mathrm{H[CuBr_2(}S\text{-}\mathrm{PEPDAH)]} \tag{1}$$

$$\underset{\text{(Monomeric complex)}}{2\ \mathrm{H[CuBr_2(}S\text{-}\mathrm{PEPDAH)]}} \underset{+\ 4\mathrm{HBr}}{\overset{-\ 4\mathrm{HBr}}{\rightleftharpoons}} \underset{\text{(Helicate)}}{(\mathrm{M})\text{-}[\mathrm{Cu(}S\text{-}\mathrm{PEPDA)]_2}} \tag{2}$$

The molecular structure of (*M*)-[Cu(*S*-PEPDA)]$_2$ has been determined by X-ray crystallography§ and the ORTEP plot is depicted in Fig. 1(a). The helicate structure is comprised of two copper(II) ions and two doubly deprotonated amide ligands, *S*-PEPDA^{2-}. Each *S*-PEPDA^{2-} ligand coordinates to the two copper(II) ions through all five nitrogen donor atoms in such a way that each copper is coordinated to one terminal pyridine nitrogen and one carboxamide nitrogen from each of the two ligands. The two central pyridine nitrogen atoms both bridge the two copper(II) atoms. The complex has (*M*) helical chirality, presumably because the interligand repulsions between the methyl and carbonyl groups of the two interlocked ligands are minimised in this configuration.

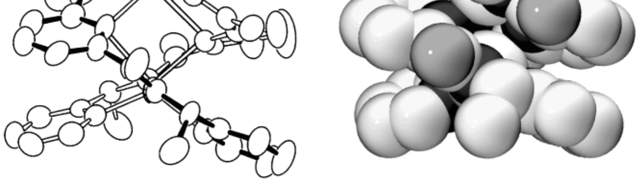


Fig. 1 (a) ORTEP plot and (b) spece filling model of the *M* helicate complex (*M*)-[Cu{(*S*)-PEPDA}]$_2$.

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† Electronic supplementary information (ESI) available: preparation of (*R*)- and (*S*)-PEPDAH$_2$. See http://www.rsc.org/suppdata/cc/b2/b202700c/

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Interestingly, the lone pair electrons of the central pyridine nitrogen atoms are directed toward the center of the Cu(II)···Cu(II) vector. The distance between copper atoms is 3.5294(7) Å. Two Cu(II) atoms and two nitrogen atoms of the bridging pyridine form a distorted square. The angles of the distorted square are between 88.0(1) and 91.9(1)° and the lengths of the four sides are between 2.245(4) and 2.713(4) Å. The angles between this plane and the planes of bridging pyridines are 71.891 and 107.102°. The Cu–N deprotonated amide bond lengths are between 1.914(3) and 1.958(3) Å. The relatively long bonds between the copper atoms and the terminal pyridine nitrogen atoms (2.046(4)–2.265(4) Å) indicate the d_{z^2} ground state for this molecule.

The helicate formation process involves the complementary aggregation of two ligands with the same configurations at carbon. Thus, treatment of a 1:1 mixture of *S*- and *R*-PEPDA with $CuBr_2$ in the presence of triethylamine produces a racemic mixture of the helicates, (*M*)-[Cu(*S*-PEPDA)]$_2$ and (*P*)-[Cu(*R*-PEPDA)]$_2$ quantitatively. This indicates that a self-recognition process takes place during helicate formation just as self-recognition through complementary hydrogen bonding is involved in the double strand formation of DNA.

Fig. 2 shows the circular dichroism spectra of (*M*)-[Cu(*S*-PEPDA)]$_2$. The intensity of the CD spectrum for the helicate is enhanced in all regions compared to the monomer. This phenomenon can be understood from the difference between the monomer and the helicate. By monitoring the changes that occur in the CD spectrum, it can be shown that the addition of one equivalent of HBr results in the breakdown of the helicate structure with the exclusive formation of the mononuclear complex H[Cu(II)Br$_2$(*S*-PEPDAH)]. Upon addition of excess HBr the free ligand is liberated from the mononuclear complex.

In conclusion, we have found that the mononuclear complex {*N*,*N′*-bis[*S*-1-(2-pyridyl)ethyl]pyridine-2,6-dicarboxamido}-copper(II) undergoes reversible conversion to a dinuclear, chiral helicate. The helicate formation, which is controlled by the removal or addition of HBr, involves a self-recognition feature such that only the (*M*)-*S*,*S* and (*P*)-*R*,*R* helicates are formed from a racemic mixture of the carboxamide ligand and $CuBr_2$. In this sense the helicate formation process resembles the reversible double helix formation of DNA. It is noteworthy that for these complexes breakdown of the helicate proceeds much faster than the helicate assembly process.

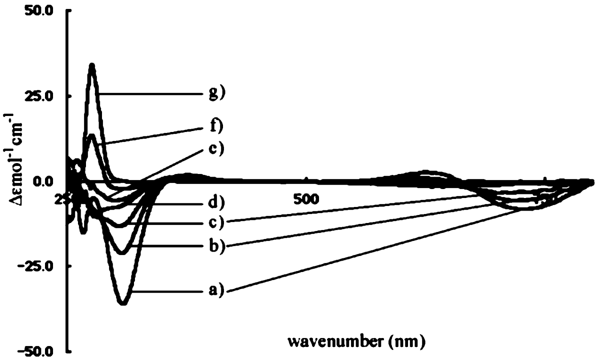

Fig. 2 CD spectrum change of (*M*)-[Cu(*S*-PEPDA)]$_2$ in methanol with addition of HBr: (a) 0, (b) 0.1, (c) 0.2, (d) 0.4, (e) 0.6, (f) 1.0 (g) 2.0 equiv.

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Notes and references

‡ *S*-PEPDAH$_2$ was prepared from a 1:2 ratio of 2,6-pyridinecabonyl dichloride and (*S*)-(pyridyl)ethylamine almost quantitatively (yield 88%) and details are submitted as ESI.†

§ *Crystal data*: for (*M*)-[Cu{(*S*)PEPDA}]$_2$·CH_2Cl_2: $Cu_2C_{43}H_{40}N_{10}O_2$, M_r = 926.85, green blocks, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 14.804(2), b = 16.226(3), c = 17.416(3) Å, V = 4183(1) Å^3, $F(000)$ = 1904.00, Z = 4, D_c = 1.471 g cm^{-3}, μ(Mo-Kα) = 11.95 cm^{-1}. Crystal dimensions: 0.20 × 0.20 × 0.20 mm. A total of 13420 reflections were collected, 9297 unique (R_{int} = 0.106). The structure was solved by direct method (SHELX-97), and developed through subsequent cycles of least squares refinement and difference Fourier synthesis, final $R1$ = 0.068 and R_w = 0.105 for 7825 reflutions ($I > 2\sigma(I)$) with a GOF of 1.23. Data were measured on a Rigaku/MSC mercury CCD diffractometer with graphite monochromatized Mo-Kα radiation.

For H[CuBr$_2$(*S*-PEPDAH)]: $CuC_{21}H_{21}Br_2N_5O_2$: M_r = 598.78, green blocks, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 10.716(7), b = 11.405(7), c = 17.92(2) Å, V = 2190(2) Å^3, $F(000)$ = 1188.00, Z = 4, D_c = 1.816 g cm^{-3}, μ(Mo-Kα) = 46.86 cm^{-1}. Crystal dimensions: 0.20 × 0.20 × 0.10 mm. A total of 16671 reflections were collected, 4844 unique (R_{int} = 0.089). The structure was solved by direct method (SIR 92), and developed through subsequent cycles of least squares refinement and difference Fourier synthesis, final $R1$ = 0.073 and R_w = 0.195 for 4496 reflutions ($I > 2\sigma(I)$) with a GOF of 1.28. Data were measured on a Rigaku/MSC mercury CCD diffractometer with graphite monochromatized Mo-Kα radiation.

For racemic-(*P*/*M*)-[Cu(PEPDA)]$_2$·5H_2O:_ $Cu_2C_{42}H_{50}N_{10}O_{10}$, M_r = 982.01, green blocks, triclinic, space group $P1$ (no. 2), a = 10.483(1), b = 12.709(1), c = 17.889(2) Å, α = 83.592(10), β = 79.837(9), γ = 67.482(7)°, V = 2164.5(4) Å^3, $F(000)$ = 1020.00, Z = 2, D_c = 1.507 g cm^{-3}, μ(Mo-Kα) = 10.53 cm^{-1}. Crystal dimensions: 0.20 × 0.20 × 0.20 mm. A total of 21352 reflections were collected, 9348 unique (R_{int} = 0.028). The structure was solved by direct method (SIR92), and developed through subsequent cycles of least squares refinement and difference Fourier synthesis, final $R1$ = 0.044 and R_w = 0.110 for 7142 reflutions ($I > 2\sigma(I)$) with a GOF of 1.04. Data were measured on a Rigaku/MSC mercury CCD diffractometer with graphite monochromatized Mo-Kα radiation.

CCDC reference numbers 182239–182241. See http://www.rsc.org/suppdata/cc/b2/b202700c/ for crystallographic data in CIF or other electronic format.

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