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Molecular self-assembly: diastereoselective synthesis and structural characterisation of a novel binuclear copper(I) double helicate †

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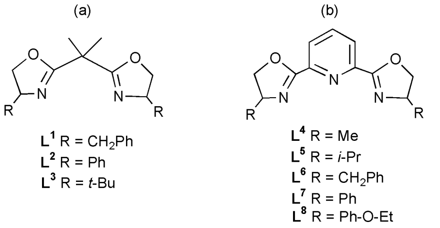
The reaction of copper(I) trifluoromethane sulfonate, $CuCF_3SO_3{\cdot}0.5C_6H_6$ with 2,6-bis[(4*S*)-4-*i*-propyl-1,3-oxazoline-2-yl]pyridine *S,S*-**L**^{5} in acetonitrile gives the binuclear bis[{2,6-bis[(4*S*)-4-*i*-propyl-1,3-oxazoline-2-yl]pyridyl}-copper(I)] trifluoromethane sulfonate **1**, at room temperature. X-Ray crystallographic analysis shows that the unit cell consists of two distinct chiral binuclear structures, the cations of which represent a double-helical right-handed diastereomer (*P*), with the helical axis passing through the two copper centres. Spectroscopic data suggest the existence of the double helicate also in solution.

Introduction

The chemistry of spontaneously self-assembled supramolecular architectures based primarily on transition metal complexes is currently an active and a rapidly expanding research area. Various forms of these highly organised structures have been extensively described in the literature.[1–5] Mainly due to their similarity with nucleic acids,[6] polynuclear transition metal double helicates[3,7,8] have attracted particular attention. In this context, Cu^I and Ag^I helicates are among the best investigated structures.[9–23] By using an enantiomerically pure ligand, Lehn and co-workers have synthesised trinuclear metal complexes with high induction of helical chirality.[24] Since publication of this work a number of reports that are directed at stereoselective formation of helicates have appeared in the literature.[13,16,25] Helicates also have a wide range of interesting applications including catalysis.[3]

In the course of our continued efforts aimed at finding effective chiral transition metal complexes which catalyse the enantioselective allylic peroxidation of prochiral cyclic olefins with *t*-butyl hydroperoxide as the oxidant, we have recently discovered the *in situ* generated chiral copper complex derived from cuprous trifluoromethane sulfonate and enantiomerically pure 2,6-bis[(4*S*)-4-*i*-propyl-1,3-oxazoline-2-yl]pyridine[26] *S,S*-**L**^{5} to be the most promising catalyst, among a series of other chiral copper complexes, yielding optically active products with up to 84% ee.[27]

In order to gain more insight into the reaction mechanism, and in particular to account for the actual catalytically active species that is responsible for the high enantioselectivity, we set out to investigate the structure of the independently synthesised Cu^I-*S,S*-**L**^{5} complex in detail. Metal complexes of oxazoline ligands are known and the structures of a silver(I)[12] and copper(I)[28] complex of some chiral bidentate bis(oxazoline) (box) ligands **L**$^{1–3}$ (Scheme 1, (a)) have been reported as helical co-ordination polymers. Ag^I complexes of enantiomerically pure tridentate bis(oxazoline)pyridine (pybox) ligands **L**$^{4,6–8}$ (Scheme 1, (b)) have been reported in a recent study as dinuclear double helicates or (depending on conditions) as a circular helicate in the case of Ag-*R,R*-**L**^{7} complex.[15,16] Very recently, another copper(I)-complex of a bidentate chiral box ligand has been described as a triple helicate.[28b]



Scheme 1 Selected (a) bis(oxazoline) or box ligands and (b) bis(oxazoline)-pyridine or pybox ligands.

However, to our knowledge, there is no previous report of an isolated copper(I)-complex of enantiomerically pure tridentate pybox ligands of the type **L**$^{4–8}$. Herein we report the diastereoselective synthesis and solid state structure of the isolated Cu^I-*S,S*-**L**^{5} complex that is an unusual chiral, non-racemic, double helicate binuclear complex and discuss its interesting solution properties which might be relevant to its distinct catalytic behaviour.

Results and discussion

When we treated a solution of cuprous trifluoromethane sulfonate, $CuCF_3SO_3{\cdot}0.5C_6H_6$ in dry acetonitrile with an equimolar amount of the enantiomerically pure ligand *S,S*-**L**^{5} under nitrogen at room temperature, a deep red solution resulted immediately, which on solvent removal gave a reddish brown, crystalline product **1** in 90% yield (eqn. 1).

The product was re-crystallised from pentane–THF to furnish red needles.

Single crystals of **1** suitable for X-ray crystal structure analysis were grown by slow diffusion of a concentrated solution of the complex in acetone into an ether layer after 2–4 days. The unit cell of complex **1** consists of two

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† In memory of Professor Dr. Drs. h.c. mult. Alfred Rieche (1902–2001).

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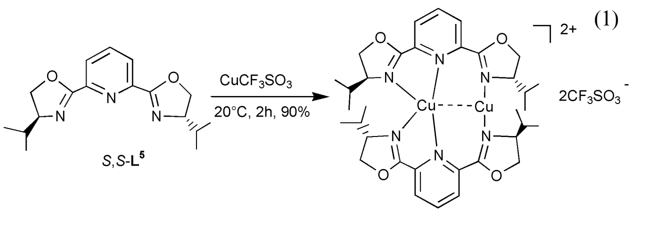
Table 1 Selected bond distances (Å) and bond angles (°) for **1**

1a		**1b**	
Cu(1)–N(6)	1.995(9)	Cu(3)–N(8)	1.989(10)
Cu(1)–N(2)	2.050(8)	Cu(3)–N(9)	2.017(9)
Cu(1)–N(1)	2.084(8)	Cu(3)–N(10)	2.123(8)
Cu(1)–N(4)	2.184(8)	Cu(3)–N(7)	2.241(9)
Cu(1)–Cu(2)	2.754(2)	Cu(3)–Cu(4)	2.734(2)
Cu(2)–N(3)	1.896(8)	Cu(4)–N(12)	1.881(9)
Cu(2)–N(5)	1.904(9)	Cu(4)–N(11)	1.897(12)
N(6)–Cu(1)–N(2)	131.1(3)	N(8)–Cu(3)–N(9)	133.7(4)
N(6)–Cu(1)–N(1)	122.7(3)	N(8)–Cu(3)–N(10)	117.9(4)
N(2)–Cu(1)–N(1)	81.5(3)	N(9)–Cu(3)–N(10)	81.8(4)
N(6)–Cu(1)–N(4)	79.7(4)	N(8)–Cu(3)–N(7)	78.5(4)
N(2)–Cu(1)–N(4)	108.1(3)	N(8)–Cu(3)–N(4)	109.0(3)
N(5)–Cu(2)–N(3)	163.3(4)	N(12)–Cu(4)–N(11)	167.9(4)



1

crystallographically distinct molecules **1a,b**[29] of independent symmetries that share the same constitution and crystallise in the monoclinic crystal system (Fig. 1). Important bond distances and bond angles are summarised in Table 1.

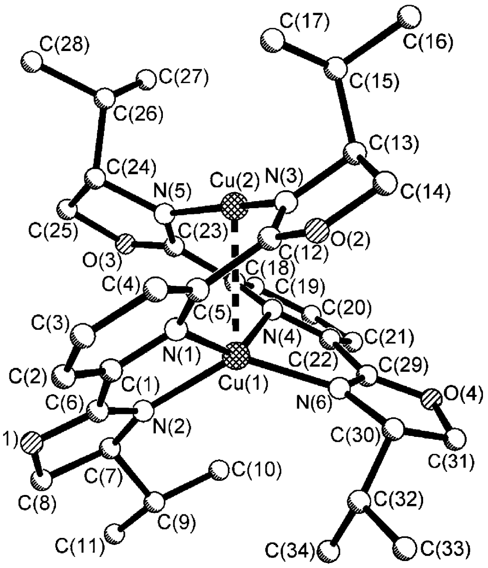


Fig. 1 Crystal structure of the cation of **1a**. A view of the cation $[Cu_2(S,S\text{-}L^5)_2]^{2+}$, perpendicular to the Cu–Cu axis. The trifluoromethane sulfonate anions and hydrogen atoms were omitted for clarity. The structure of the cation of **1b** is very similar.

In both molecules of the elementary cell two ligand molecules are bound to two copper centres. In each dimeric molecule the two copper ions have different co-ordination environments. One Cu ion is nearly linearly co-ordinated to two imine nitrogens, one from each ligand whereas the nitrogen atoms of the two pyridine rings and the remaining two imine nitrogens forming the oxazoline rings bind the other Cu ion in a quasi tetrahedral fashion. The torsional angles between oxazoline domains to which the 'linear' copper ions co-ordinate deviate from orthogonality by *ca.* 10° (∠C(24)–N(5)–N(3)–C(13) = 82.25°, **1a**; ∠C(42)–N(11)–N(12)–C(65) = 80.08°, **1b**) whereas those between the planes described by the pyridine rings and the oxazoline moieties make angles of around 30° (*e.g.* ∠N(4)–C(18)–C(23)–N(5) = 29.26°, **1a**; ∠N(10)–C(56)–C(63)–N(12) = 33.29°, **1b**). In other words, one oxazoline ring of each ligand rotates about the C–C bond (*e.g.* C(5)–C(12) and C(18)–C(23) in Fig. 1) connecting it to the pyridine ring such that the N atoms face closest to the nearby copper atom for co-ordination. As a consequence, in both molecules **1a** and **1b**, the complex is forced to adopt a double helical conformation that is generated by the twisting of the ligands around the metal ions, with the helical axis collinear with the line joining the two copper centres and the *i*-propyl groups projecting away from the helical axis (Fig. 2).

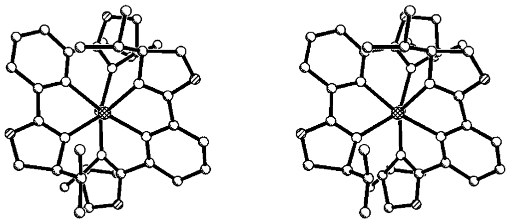


Fig. 2 Stereoscopic view of the cation of **1a**, $[Cu_2(S,S\text{-}L^5)_2]^{2+}$, looking along the Cu–Cu helical axis.

In eqn. 1 the double helicate **1** is represented in planar form merely to emphasise the co-ordination pattern. All Cu–N bonds to the two co-ordinate copper are much shorter than those at the four co-ordinate copper atom. Thus, the average Cu–N distances for two co-ordinate copper atoms are 1.899 and 1.889 Å while the Cu–N distances for the four co-ordinate copper are 2.078 and 2.092 Å in molecules **1a** and **1b**, respectively. Moreover, while the Cu–N bonds to the two co-ordinate copper are nearly orthogonal to the helical axis (average CuCuN angles 88.72 (**1a**) and 88.23° (**1b**)), for the four co-ordinate copper this angles range from 66.79 to 119.64° in **1a** and from 66.98 to 116.83° in **1b**.

Since the free ligand is enantiomerically pure (S,S-$\mathbf{L}^5$) the resulting complex is expected to possess either the (*P,S,S*) or (*M,S,S*) configuration. Careful examination of molecular models suggested the existence of destabilising steric interactions between the *i*-propyl groups at the stereogenic carbon centres in the case of the (*M,S,S*) isomer and predicted the favoured formation of the (*P,S,S*) isomer[30] which is in full agreement with the observed result. Such interactions have often been suggested to explain the high chiral inductions observed in related complexes.[13,15,24]

Significant differences between the two molecules are mainly the Cu–Cu and Cu–O distances, Cu–N bond lengths and ∠N–Cu–N bond angles (see Table 1). The Cu–Cu distances in **1a** and **1b** are 2.754 and 2.734 Å respectively. Since this distance is greater than twice the atomic radius of the copper atom[31] we consider it as a weak intramolecular interaction rather than a real Cu–Cu chemical bond. However, the Cu–Cu distances given here fall exactly within the range reported (2.639(2)–2.938(2) Å)[32] in a recent spectroscopic study that claims evidence for the existence of Cu–Cu bonding interaction in binuclear Cu^I complexes. But these are significantly shorter than the reported Cu–Cu distances of 2.821(5)–2.854(2) Å for binuclear double helicates with *1H*-benzimidazole ligands[9c,33] and the Ag–Ag distance of 2.985(2) Å reported[15] for the closely related Ag^I-complex $[Ag_2(S,S\text{-}L^6)_2]^{2+}$. A shorter Cu–Cu distance of 2.626(1) Å was also previously interpreted as a chemical bond in a dinuclear Cu^I complex of a Schiff-base ligand.[34] The Cu–O distances between the trifluoromethane sulfonate ions around the 'linear' copper are significantly different (2.382 Å in molecule **1a** *versus* 2.504 Å in molecule **1b**). This suggested the existence of a weak bond between the 'linear' copper and the trifluoromethane sulfonate anion. If this contact is taken into account the geometry around this particular Cu^I ion becomes trigonal, although the C–N bond distances of 1.881–1.902 Å reported here are typical for two co-ordinate Cu^I complexes.[28] The shorter Cu–O contact distance in molecule **1a** is also reflected in the smaller N–Cu–N bond angle (∠N(5)–Cu(2)–N(3) = 163.3(4), **1a** *versus* ∠N(11)–Cu(4)–N(12) = 167.9(4), **1b**) that represents a more considerable deviation of the bond angle from linearity. An interesting feature of this structure is the assembly of the dimeric units by extensive non-bonding interactions of two $[Cu_2(S,S\text{-}\mathbf{L}^5)_2]^{2+}$ molecules (not shown in Fig. 1). The contact between the two double helical cations $[Cu_2(S,S\text{-}\mathbf{L}^5)_2]^{2+}$ appears to be mediated by a 'bridging' triflate ion with one oxygen atom that is located nearly equidistant from one of the CH_2 protons of the oxazoline ring on one dimer (C–H ··· O = 2.451 Å) and the pyridine proton at C-4 on the other (C–H ··· O = 2.434 Å). There are also additional, weaker interactions (C–H ··· F[35] and C–H ··· O hydrogen bonds) that may be accountable for holding the two dimeric units of $[Cu_2(S,S\text{-}\mathbf{L}^5)_2]^{2+}$ together. The two molecules are arranged such that the dihedral angle between the Cu–Cu axes is *ca.* 107°, that is in sharp contrast to the related binuclear complex prepared from 2,6-bis(1-methyl-imidazol-2-yl)-pyridine[33] in which the crystallographic two-fold axis passes through all four copper atoms, in two crystallographically non-equivalent molecules.

Spectroscopic properties of complex 1

FT IR spectroscopy. The FT IR spectrum of *S,S*-$\mathbf{L}^5$ shows characteristic bands at 1569 and 1637 cm^{-1} which we assign to the pyridine ring and imine C=N stretch respectively.[21] In the spectrum of **1** these bands are shifted to higher energies at 1581 and 1648 cm^{-1} respectively which agrees with co-ordination of the metal to the nitrogen donor atoms. The typical strong bands due to stretching vibrations of the $CF_3SO_3^-$ ions appear at 1263, 1224, 1159, and 1031 cm^{-1}. Co-ordination of the $CF_3SO_3^-$ ions to copper centres is not evident from the spectrum.[36]

UV/Vis spectroscopy. The UV/Vis spectrum of *S,S*-$\mathbf{L}^5$ in methanol shows unresolved bands in the UV region around λ = 250 nm (ε = 1.8911 × 10^4 M^{-1}cm^{-1}) and λ = 286 nm (ε = 1.0335 × 10^4 M^{-1}cm^{-1}). Complex **1** shows broad bands at λ = 234 nm (ε = 1.01452 × 10^5 M^{-1}cm^{-1}), λ = 285 nm (ε = 4.7534 × 10^4 M^{-1}cm^{-1}), λ = 330 nm (ε = 5.25 × 10^3 M^{-1}cm^{-1}), λ = 339 nm (ε = 9.5673 × 10^4 M^{-1}cm^{-1}) and λ = 399 nm (ε = 2.32 × 10^3 M^{-1}cm^{-1}). These data also demonstrate the co-ordination of the metal to the ligand.

Chiroptical properties. Polarimetric investigation of **1** showed a specific rotation that is positive yet unreliably too small to report compared to the specific rotation of the free ligand ($[\alpha]_D^{20}$ = −121 (*c* = 0.7, CH_2Cl_2)).

The CD spectrum of *S,S*-$\mathbf{L}^5$ shows negative Cotton effects in the UV region at λ = 233 nm ($\Delta\varepsilon$ = −3.41 M^{-1} cm^{-1}) and a weaker band at λ = 283 nm ($\Delta\varepsilon$ = −1.15 M^{-1} cm^{-1}). Complex **1** on the other hand shows a weak but very broad positive Cotton effect around λ = 398 nm ($\Delta\varepsilon$ = +1.8 M^{-1}cm^{-1}) and a negative Cotton effect at λ = 302 nm ($\Delta\varepsilon$ = −1.34 M^{-1} cm^{-1}) as well as large positive and negative Cotton effects of comparable intensities but of opposite signs at λ = 269 nm ($\Delta\varepsilon$ = +9.16 M^{-1} cm^{-1}, and λ = 236 nm ($\Delta\varepsilon$ = −7.47 M^{-1} cm^{-1}) in the UV region respectively, which we believe are due to exciton coupling accompanying the π–π* CT transitions.[37] The value $\Delta\varepsilon_{269}$ = +9.16 M^{-1}cm^{-1} is comparable to that reported for the related silver(I) helicate $(Ag_2(S,S\text{-}\mathbf{L}^6)_2]^{2+}$, $\Delta\varepsilon_{301}$ = +10.15 M^{-1}cm^{-1}).[15] Thus, the data strongly suggest (a) the selective formation of a single diastereomer; (b) the existence of the helical structure in solution with the sign of the band at λ = 269 nm corresponding to the helical screw sense in accord with the solid state structure.[13,37]

ES mass spectrometry. The positive mode electron spray mass spectrum of isolated **1** varied considerably depending on the solvent and concentration. In acetonitrile two intense peaks appear at *m*/*z* = 364 and *m*/*z* = 665 with nearly equal intensities. These peaks correspond to the masses of the cations $[Cu_n(S,S\text{-}\mathbf{L}^5)_n]^{n+}$ (*n* = 1, 2) and $[Cu(S,S\text{-}\mathbf{L}^5)_2]^+$ respectively. Careful analysis of the peak pattern at *m*/*z* = 364 showed that the typical Δ*m*/*z* = 0.5 peak separations found in a doubly charged species are missing in sharp contrast to the case reported by Williams *et al.*[15,16] for the related $[Ag_2(S,S\text{-}\mathbf{L}^6)_2)]^{2+}$ complex. The isotopic distribution pattern agrees well with the one calculated for the monocationic species $[Cu(S,S\text{-}\mathbf{L}^5)]^+$ suggesting that either the monomeric structure is more stable in this solvent, or this species results from fragmentation in the mass spectrometer. Additional small peaks were detected at *m*/*z* = 404 $[Cu(S,S\text{-}\mathbf{L}^5)(CH_3CN)]^+$ in acetonitrile suggesting a complex equilibrium in solution with the participation of the solvent. On the other hand, if acetone is used as the solvent then three peaks centred at *m*/*z* = 364.1 $[Cu_n(S,S\text{-}\mathbf{L}^5)_n]^{n+}$ (100%), *m*/*z* = 665.3 $[Cu(S,S\text{-}\mathbf{L}^5)_2]^+$ (42%), and *m*/*z* = 877.2 $[Cu_2(S,S\text{-}\mathbf{L}^5)_2(CF_3SO_3)]^+$ (45%), are detectable (see Fig. 3a). The calculated spectra of the latter two species are in excellent accord with the experimental data.

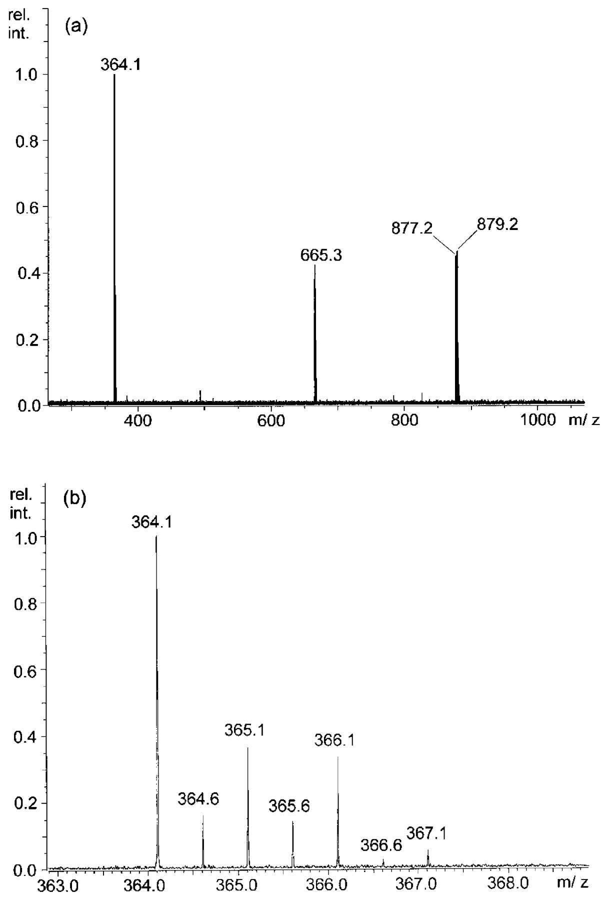


Fig. 3 ES-MS of **1** (a) full spectrum; (b) enlargement of the peak corresponding to $[Cu_2(S,S\text{-}\mathbf{L}^5)_2]^{2+}$. The solvent is acetone.

Comparison of the simulated spectra of the species $[Cu(S,S\text{-}\mathbf{L}^5)]^+$ and $[Cu_2(S,S\text{-}\mathbf{L}^5)_2]^{2+}$ with the experimental peak at *m*/*z* = 364 revealed that the latter represents a 1.5 : 1 mixture of these species respectively (Fig. 3). This ratio is nearly reversed (1 : 1.3) when a solvent mixture of $CHCl_3$–CH_3CN–HCO_2H was used. Therefore, these results confirm the existence of the double helicate under experimental conditions.

Table 2 Comparison of ^{1}H and ^{13}C NMR data[a] of the free ligand *S,S*-**L**^{5} and the complex **1** in acetone-d$_6$

^{1}H-NMR		^{13}C-NMR	
S,S-**L**$_5$[b]	**1**[c]	*S,S*-**L**^{5}[b,d]	**1**[d]
8.18 (d, $J = 7.7$, 2H, H$_{py}$)	8.61 (dd, $J = 7.5, 7.3$, 1H, H$_{py}$)	163.25	168.54
8.00 (‘t’, $J = 7.5$, 1H, H$_{py}$)	8.48 (d, $J = 7.5$, 2H, H$_{py}$)	148.31	144.25
4.50 (dd, $J = 8.4, 9.0$, 2H, OCH)	5.14 (‘t’, $J = 9.5$, 2H, OCH)	138.30	142.81
4.24–4.07 (m, 4H, 2 × OCH + 2 × NCH)	4.84 (‘t’, $J = 9.0$, 2H, OCH)	126.56	128.99
1.80 (m, 2H, Me$_2$-CH)	4.32 (ddd, $J = 9.4, 9.2, 5.0$,2H, NCH)	73.74	75.34
1.01 (d, $J = 6.6$, 6H, 2 × CH$_3$)	1.92 (m, 2H, Me$_2$-CH)	71.49	71.27
0. 93 (d, $J = 6.6$, 6H, 2 × CH$_3$)	0.78 (2 × d, $J = 7.0, 6.5$, 12H, 4 × CH$_3$)	33.73	32.04
		18.99	18.37
		18.74	17.49

[a] δ in ppm, J in Hz. [b] 300 MHz, authentic sample. [c] 500 MHz, the data are for one ligand unit (see discussion in text). [d] 75 MHz.

NMR spectroscopy. Both the ^{1}H and ^{13}C NMR spectra of complex **1** are made up of sharp signals indicative of the presence of a single species and the symmetrical nature of the molecule in solution. In both cases the expected numbers of signals of the equivalent groups in the free ligand (C_2 symmetric) are also observed in the spectrum of the complex (Table 2).

In the ^{1}H NMR spectrum of **1**, all signals of ring protons are shifted to lower fields compared to those of the free ligand. The signals of the CH$_2$ groups forming the oxazoline rings appear as pseudo triplets. The low-field shift is also observed for the signals of pyridine protons which suggested the complexation of the copper ions at the nitrogens of the chelating ligand. In particular the strong low-field shift observed for the pyridine proton at the 4-position ($\Delta\delta$ = 0.61 ppm) implies the coordination of metal at the N atom of the pyridine ring. Lowering the temperature to 200 K had no significant effect on the spectrum.

The ^{13}C NMR spectrum also shows a very similar situation. All (and only) the nine ^{13}C signals detected for the free ligand could be measured for the complex as well, confirming the symmetric nature of the complex in solution. However, if the complex exists in solution as "fixed" in Fig.1 in a significant proportion one would expect 17 ^{13}C-signals rather than the 9 signals recorded (Table 2). However, if rapid exchange between the pyridine rings occurs on the NMR time-scale following relaxation of the structure in solution the bimetallic complex in this case becomes D_2 symmetrical[9f,12,13] and the number of ^{13}C-signals will be averaged to 9 in support of the twofold positive charged double helical species [Cu$_2$(*S,S*-**L**^{5})$_2$]$^{2+}$. In an attempt to freeze this exchange we recorded ^{13}C NMR at 173 K in THF–d$_8$-acetone–d$_6$ mixture. The spectrum is nearly identical to the one at room temperature which means that the exchange is very fast even at this temperature. Thus, assuming that not all ^{1}H and ^{13}C NMR signals of several species overlap accidentally, examination of the NMR spectra shows that only one species is present in solution.

Conclusion

In summary we have synthesised the first binuclear copper(I) pybox complex **1** diastereoselectively by the reaction of $CuCF_3SO_3{\cdot}0.5C_6H_6$ with 2,6-bis[(4*S*)-4-*i*-propyl-1,3-oxazolin-2-yl]-pyridine *S,S*-**L**^{5} in acetonitrile at room temperature. Complex **1** was isolated and structurally characterised. Analysis of the X-ray crystal structure demonstrates that the unit cell consists of two crystallographically distinct molecules which are held together by weak, non-bonding intermolecular interactions. Each of the molecules is a right-handed double helicate with the helical axes collinear with the straight line connecting copper centres. CD specroscopy as well as structural models suggest the existence of the *P* double helicate also in solution.[13,37]

Experimental

General

^{1}H NMR spectra were recorded on a Varian Gemini 300 (300 MHz) spectrometer or a Varian Unity 500 (500 MHz) spectrometer. Chemical shifts (δ values) are given in ppm. The following abbreviations are used: d = doublet, m = multiplet, t = triplet, ‘t’ = pseudo triplet. Specific rotation measurements were carried out with a Perkin-Elmer 341 polarimeter; $[\alpha]_D$, λ = 589 nm, c in g (100 ml)$^{-1}$. CD spectra were measured on a JASCO J-715 spectrometer in a 0.2 cm quartz cell filled with 1.00×10^{-4} M (*S,S*-**L**^{5}), 1.36 10^{-4} M (**1**) sample solutions in methanol at 23 °C. ES-MS spectra were taken using an APEX II ESI-FT-ICR-MS equipment of Bruker Daltronics. An IR spectrum was obtained from a KBr pellet on a Philips PU 9600 FT-IR spectrometer. A Beckman Du 650 spectometer was used for the UV/Vis spectra. CHNS-analyses were conducted on a LECO CHNS-932 equipment. The copper value was determined from an acid digested solution of the complex with a Philips PU 7000 AES spectrometer using standard copper solutions. Acetonitrile was distilled under N$_2$ from CaH$_2$ prior to use. Acetone was freshly distilled from P$_4$O$_{10}$ under N$_2$, Chloroform was purchased as 99% from Jansen and was filtered over basic alumina before use. Cuprous trifluoromethane sulfonate, $CuCF_3SO_3{\cdot}0.5C_6H_6$ and the ligand *S,S*-**L**^{5} were purchased from Fluka and were used without further purification.

Synthesis of complex 1

459 mg (1.659 mmol) cuprous trifluoromethane sulfonate, $CuCF_3SO_3{\cdot}0.5C_6H_6$ and 500 mg (1.659 mmol) ligand *S,S*-**L**^{5} were mixed in 10 ml dry acetonitrile under N$_2$. This resulted in immediate formation of a reddish brown solution. The reaction mixture was stirred for a further 2 h at ambient temperature. After filtration of the mixture on a thin Celite layer and solvent removal under reduced pressure a reddish brown solid was isolated which was re-crystallised from THF–pentane to furnish red crystals of **1**, soluble in acetone, chloroform, and acetonitrile. Yield: 767 mg, 90%. Mp (acetone–ether) 249–252 °C. Found: C, 43.09; H, 4.83; N, 7.91; S, 6.14; Cu, 12.20; $C_{36}H_{46}Cu_2F_6N_6O_{10}S_2$ requires C, 42.10, H, 4.48, N, 8.18, S, 6.20; Cu, 12.37%. λ_{max}/nm (MeOH) 231 (ε/dm^3 mol^{-1} cm^{-1} 104786), 234 (101452), 285 (47534), 330 (5250), 339 (95673), 399 (2320). ν_{max}/cm^{-1} 1648s, 1581s, 1263s, 1159s and 1031s. ^{1}H and ^{13}C NMR: See Table 2. ES-MS (+ mode, acetonitrile): *m/z* = 665.3 ([Cu(*S,S*-**L**^{5})$_2$]$^+$, 100%), 364.3 ([Cu(*S,S*-**L**^{5})]$^+$, 92), 404.7 ([Cu(*S,S*-**L**^{5})MeCN]$^+$, 18). ES-MS (+ mode, acetone): *m/z* = 364.1 ([Cu(*S,S*-**L**^{5})]$^+$, [Cu$_2$(*S,S*-**L**^{5})$_2$]$^{2+}$, 100%), 665.3 ([Cu(*S,S*-**L**^{5})$_2$]$^+$, 42), 877.2 ([Cu$_2$(*S,S*-**L**^{5})$_2$(CF$_3$SO$_3$)]$^+$, 45).

X-Ray crystal structure determination of 1

Single crystals suitable for X-ray crystallographic analyses of **1** were obtained by slow diffusion of a concentrated solution of

Table 3 Crystal data and structure refinement for **1**

Formula	$C_{36}H_{46}Cu_2F_6N_6O_{10}S_2$
M	1027.99
T/K	293(2)
Crystal system	Monoclinic
Space group	$P2$
a/Å	14.560(3)
b/Å	10.193(2)
c/Å	30.500(6)
α/°	90.00
β/°	90.48(3)
γ/°	90.00
V/Å^3	4526(2)
Z	4
μ/mm^{-1}	1.115
Reflections collected	19463
Independent reflections/R_{int}	13556/0.0417
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	13552/1/1122
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0793$, $wR2 = 0.1798$
R indices (all data)	$R1 = 0.1120$, $wR2 = 0.2178$

$R = \Sigma/|F_o| - [|F_c|]/\Sigma|F_o|$. $wR = [\Sigma w(F_o^2 - F_c^2)/\Sigma wF_o^4]^{1/2}$.

the complex in acetone into an ether layer after several days. Details of data collection and processing, structure analysis and data refinement are summarised in Table 3.

Diffraction experiments were performed on an AXS-SMART area detector diffractometer (ω rotation scans with narrow frames) equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data sets were corrected for Lorentz-Polarisation effects and for the effects of adsorption using the program SADABS.[38] The structure was solved by direct methods using the SHELX-97[39] computer program. All non hydrogen atoms were refined anisotropically, hydrogens were fixed in idealised positions and allowed to ride on the atoms to which they were attached. Each hydrogen atom of the CH-, CH_2-, and CH_3- groups was assigned on common isotropic manual parameter. Some of the C-atoms show high displacement factors. A splitting of these atoms in two positions gave no better R-values.

CCDC reference number 170087.

See http://www.rsc.org/suppdata/dt/b2/b201550a/ for crystallographic data in CIF or other electronic format.

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