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Self-assembly of a stereoselective trinuclear sodium/lithium triple helix†

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A new three nuclear triple-stranded helicate complex M_3L_3 containing Na^+/Li^+ ions has been synthetised and characterised by ^1H, ^{23}Na, ^7Li solution NMR, ESI-MS and X-ray crystallography.

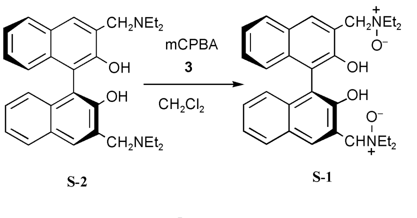
Metal assisted self-assembly of independent ligands to form helices quantitatively with labile metals represent a goal in supramolecular chemistry.[1]

We describe herein the synthesis and complexation properties of a new chiral ligand **1**, which in solution is able by self-assembly to form trinuclear helicates, in the presence of sodium or lithium triflates.

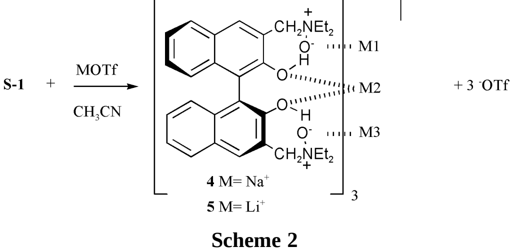
The novel N-oxide binaphthol derivative ligand **(*R*)/(*S*)-1** is produced in excellent yield in a single-step reaction from the corresponding (*R*)/(*S*)-3,3′-bis(*N*,*N*′-diethylaminomethyl)-1,1′-binaphthalenyl-2,2′-diol **2**[2] with *m*-chloroperbenzoic acid **3** in dichloromethane (Scheme 1). It was obtained as a white solid and the structure was confirmed by ^1H, ^{13}C NMR data and HRMS.

An important design consideration of this ligand is that the incorporation of amine N-oxides acts as a powerful electron-pair donor, and since chiral and optically stable binaphthol subunits are used, both *R* and *S* ligands could be obtained in enantiomerically pure form.[3]

Ligand **1** is conceptualised as a tetradentated unit (Scheme 2). The ability of ligand **1** to bind alkali metal ions as a neutral ligand was examined utilising NMR methods. Reaction of NaOTf and enantiopure **(*S*)-1** in the ratio 1 : 1 generates a single, highly symmetric, metal complex **4** as demonstrated by its ^1H NMR spectrum that contains a single set of resonances. The 1 : 1 stoichiometry of **4** was determined by NMR titration and by ESI-MS. The well defined ^1H NMR spectrum of **4** reveals that the three ligands are equivalent, as are the two halves of each ligand. The signals of the benzylic protons are shifted significantly upfield at δ 3.86, J = 13.2 Hz and δ 2.69, J = 13.2 Hz. The observation of the diastereotopic benzilic protons is certainly due to the chirality of the molecule. Under conditions of slow rotation around the $CH_2N^+–O^-Et_2$ bond, due to the metal interaction, diastereotopic ethyl chain shifts in ^{13}C and ^1H NMR spectra are expected.



Scheme 1



Scheme 2

^{23}Na NMR spectroscopy was performed to study the interaction between the ligand and sodium ions in the complex. The ^{23}Na NMR spectrum at ambient temperature consists of two broad signals at δ −1.06 and 5.69, downfield of the free Na ion at δ −4.77 (Fig. 1).

For a more clear structure analysis from the NMR point of view, the lithium complex **5** was obtained from enantiopure **(*S*)-1** and lithium triflate. Evidence for the formation of the complex **5**‡ was provided by the ^7Li NMR spectrum (Fig. 1).

The appearance of two ^7Li resonances at lower field in a 1 : 2 integral ratio is consistent with a symmetric complexation of the lithium ions by the ligand. Since the exchange between the complexed lithium and free lithium is slow on the NMR time scale, the three species can be observed on the ^7Li NMR spectrum at δ 2.23, 1.356 and 0.383; the former two are complexed and the latter corresponds to free lithium triflate.

2D Li–^1H HOESY[4] was used to elucidate a more detailed solution structure of **5**: only three types of protons have crosspeaks to Li1, Li3 and two types of protons with Li2 (Fig. 2). This spectrum shows well resolved cross-peaks between the lithium resonance and a benzylic proton, the ethyl chain and the phenol group, which imply close proximity of these protons to the lithium centers (see Fig. 3(b)). This provides strong evidence of an arrangement of magnetically equivalent ligands around the lithium cation.

Additional evidence for the formation of the complex **5** was provided by HRMS (ESI-ES).

Suitable single crystals for X-ray diffraction could be obtained for the sodium **4** and lithium **5** structures.[5]§ This give rise to the structures illustrated in Fig. 3.† The crystal structure showed complex **4** to be trinuclear in the solid state with the three metal centers almost linear, Na1–Na2–Na3 (172°), with

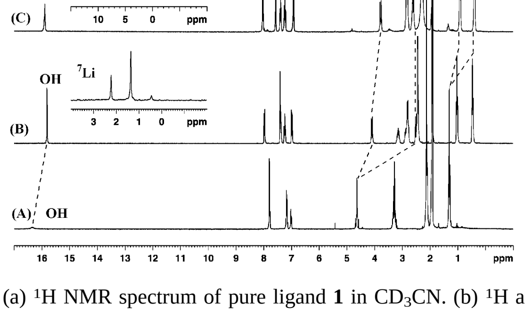


Fig. 1 (a) ^1H NMR spectrum of pure ligand **1** in CD_3CN. (b) ^1H and ^7Li NMR spectra of complex **5**. (c) ^1H and ^{23}Na NMR spectra of complex **4**.

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† Electronic supplementary information (ESI) available: (a) PDB files for **4** and **5**. (b) Experimental details. See: http://www.rsc.org/suppdata/cc/b2/b205440j/

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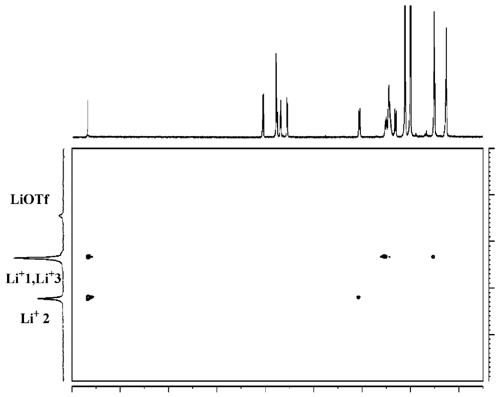

Fig. 2 2D HOESY spectrum of complex **5**. The horizontal scale represents the proton resonances of the ligand and the vertical scale represents lithium resonances of the coordinated and free lithium triflate.

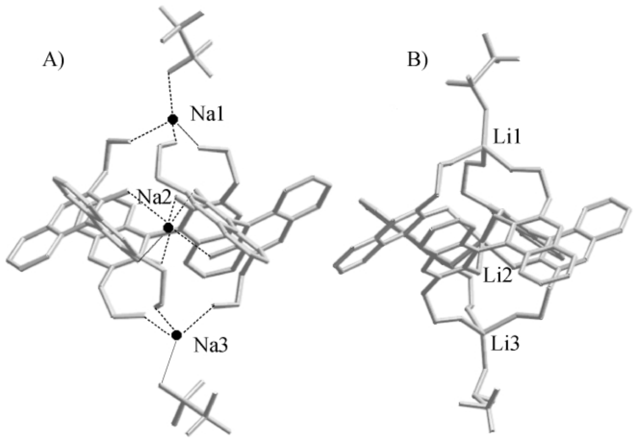

Fig. 3 (a) Molecular structure of Λ-[Na_3((***R***)-**1**)$_3$](OTf)$_3$ **4**. (b) Molecular structure of Δ-[Li_3((***S***)-**1**)$_3$](OTf)$_3$ **5**. Ethyl chains have been omitted for clarity.

intramolecular separations of 4.925 and 4.949 Å. The final refinement of complex **4** was complicated due to the high thermal motion and associated disorder of triflate groups resulting in a relatively high *R* value. The structure was well defined with respect to the metal environment and core atoms of the ligands. Each ligand unit **1** wraps around three independent sodium ions. The central atom is therefore surrounded by six oxygen atoms, with Na2–O distances of 2.378–2.471 Å. The sodium atoms Na1 and Na3 are both coordinated by three N–O at distances of 2.243–2.320 Å and by axially coordinated triflate anions at 2.451 and 2.416 Å, respectively.

Similarities between the structures of **4** and **5** are remarkable with a linear distribution in complex **5** (Li1–Li2–Li3 177°) with intramolecular separations of 4.527 and 4.619 Å. The central atom is also surrounded by six oxygen atoms, with Li2–O distances of 2.098–2.335 Å. The lithium atoms Li1 and Li3 are both coordinated by three N–O at 1.872–1.984 Å and by axially coordinated triflate anions at 1.862 and 1.984 Å, respectively.

The new ligand reported here has the ability to stack multiple cations in a linear maner. To the best of our knowledge this is the first multi-sodium/lithium triple stranded helicate obtained from a chiral ligand.

Future work in this area will be addressed to study the behaviour of other metal ions in presence of **1**,[6] as well as the role of the countrer-ion in the self-assembly process.

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Notes and references

‡ (***S***)-**1**: $[\alpha]^{25}_{589}$ −186° (*c* 0.010, CH_3CN). ^1H NMR (CD_3CN, 300 MHz), *δ* 16.40 (br s, 2H OH), 7.90–7.88 (m, 2H), 7.28–7.26 (m, 4H), 7.14–7.12 (m, 2H), 4.73 (m, 4H), 3.39 (m, 8H), 1.4 (t, 12H, *J* 7.2 Hz). ^{13}C NMR (CD_2Cl_2, 75 MHz), *δ* 156.5, 136.4, 132.8, 128.7, 127.8, 127.3, 125.3, 122.9, 122.0, 119.6, 69.5, 60.7, 60.3, 9.5, 9.2. MS (FAB$^+$) m/z 489 (MH$^+$); HRMS (FAB+): Calc. for $C_{30}H_{37}O_4N_2$: *m/z* 489.2753. Found: 489.2741.

4: $[\alpha]^{25}_{589}$ +299° (*c* 0.014, CH_3CN). ^1H NMR (CD_3CN, 300 MHz), *δ* 16.01 (s, 6H, OH), 8.14 (d, 6H, *J* 5 Hz), 7.68 (s, 6H), 7.49 (t, 6H, *J* 7 Hz), 7.33 (t, 6H, *J* 7 Hz), 7.03 (d, 6H *J* 8.4 Hz), 3.86 (d, 6H, *J* 13.2 Hz), 2.94 (m, 24H), 2.72 (d, 6H, *J* 13.2 Hz), 1.02 (t, 18H, *J* 6.9 Hz), 0.5 (t, 18H, *J* 6.9 Hz). ^{13}C NMR (CD_3CN, 75 MHz), *δ* 154.05, 135.07, 133.64, 128.39, 128.06, 127.20, 124.93, 123.27, 122.25, 118,97, 65.62, 60.91, 58.00, 7.98, 7.21. ^{23}Na NMR (CD_3CN, 79 MHz), *δ* 5.69, −1.06. ESI-MS: Calc. for $C_{92}H_{108}Na_3N_6O_{18}F_6S_2$ [M − OTf]$^+$: *m/z* 1832.6791. Found: 1832.6344.

5: $[\alpha]^{25}_{589}$ +329° (*c* 0.012, CH_3CN). ^1H NMR (CD_3CN, 300 MHz), *δ* 15.36 (s, 6H, OH), 8.08 (d, 6H, *J* 5 Hz), 7.50 (s, 6H), 7.48 (t, 6H, *J* 7 Hz), 7.35 (t, 6H, *J* 7 Hz), 7.08 (d, 6H, *J* 8.4 Hz), 3.89 (d, 6H, *J* 13 Hz), 3.05–2.87 (m, 24H), 2.72 (d, 6H, *J* 13 Hz), 1.01 (t, 18H, *J* 6.9 Hz), 0.52 (t, 18H, *J* 6.9 Hz). ^{13}C NMR (CD_3CN, 75 MHz), *δ* 153.25, 134.85, 133.88, 128.50, 128.37, 127.33, 125.18, 123.57, 122.18, 119.16, 65.35, 60.87, 57.26, 8.58, 6.88. ^7Li NMR (CD_3CN, 116 MHz), *δ* 2.230, 1.356, 0.383. HRMS (ES): Calc. for $C_{92}H_{108}Li_3N_6O_{18}F_6S_2$ [M − OTf]$^+$: *m/z* 1783.7546. Found: 1783.7593.

Pale yellow single crystals of **4** from (***R***)-**1** and colourless crystals of **5** from (***S***)-**1** were obtained by the slow evaporation of a CH_3CN solution. The crystals are of poor quality due to the triflates and solvent disorder.

§ *Crystal data* for **4**: $C_{93}H_{108}O_{21}N_6S_3F_9Na_3$, M = 1982, monoclinic, space group $P2_1/c$, a = 34.5427(11), b = 23.4946(7), c = 27.6861(9) Å, U = 22306.0(12) Å^3 , T = 298 K, Z = 8, μ = (Mo-Kα) = 0.16 mm^{-1}, 112976 reflections measured, 38987 unique R_{int} = 0.19. The final $wR2$ was 0.33 (all data).

Crystal data for **5**: $C_{93}H_{108}O_{21}N_6S_3F_9Li_3$, M = 1933.8, monoclinic, space group $P2_1/n$, a = 15.3307(10), b = 27.4036(16), c = 23.1373(14) Å, U = 9624.98(10) Å^3, T = 196 K, Z = 4, μ = (Mo-Kα) = 0.17 mm^{-1}, 60845 reflections measured, 22498 unique R_{int} = 0.155. The final $wR2$ was 0.372 (all data).

CCDC reference numbers 183483 and 183484. See http://www.rsc.org/suppdata/cc/b2/b205440j/ for cystallographic data in CIF or other electronic format.

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6 In order to prove the selectivity of the ligand **1** towards Li over Na metal ions; 28 mmol of **1** were added to a mixture of 1.1 eq. of LiOTf plus 1.1 eq. of NaOTf in 500 μl of CD_3CN: only complex **5** was detected by NMR spectroscopy.