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Expansion and Compression of a Helicate with Central Diol Units as Stereocontrolling Moieties

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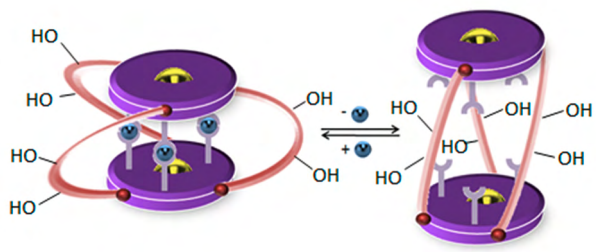

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Abstract The dicatechol ester ligand **2**-H_4 forms the compressed helicate $Li_4[(\mathbf{2})_3Ti_2]$ which upon removal of the internally bound lithium cations expands. In the compressed form, the chiral diol units control the stereochemistry of the complex which is lost upon expansion of the system.

Key words: self-assembly, helicates, molecular switches, stereochemistry

Introduction

The development of molecular switches is one important aspect in the transition of "classical" supramolecular chemistry to "functional" nanotechnology. Hereby, supramolecular chemistry closes the gap between the natural science chemistry and the technology-orientated nanosciences. Basic concepts of molecular switches have been described for several decades and were based on photoswitchable entities as well as catenanes and rotaxanes.[1]

For some years, we have been studying the expansion and compression of helicate-type coordination complexes based on the binding of internal cations which can be released upon an external stimulus (e.g. addition of a cryptand).[2] This kind of research is based on some preliminary concepts published by Yashima, who switched the length of a boran(III)-based double-stranded helicate by addition of sodium cations.[3] As an important finding, we could show that with chiral biscatechol ligands **1**-H_4, a three-state molecular switch is obtained, which allows control of the extended and compressed state of the complex, as well as of the helical twist.[2]

In the present report, we describe a related system, **2**-H_4, in which the chiral information is not located close to the complex units, but rather far away in the center of the ligand spacer (Figure 1).

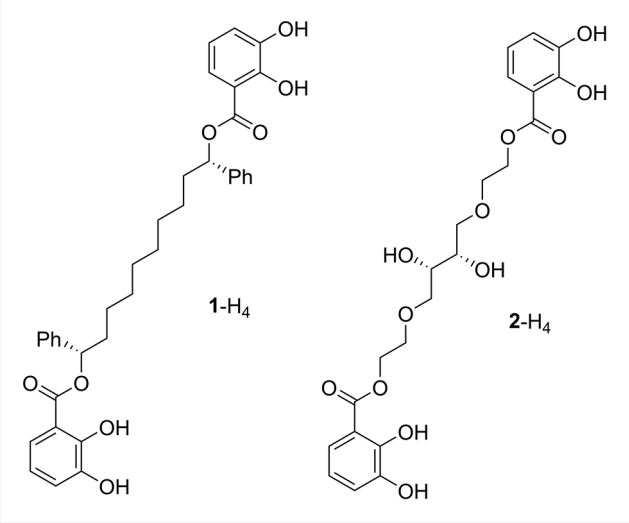
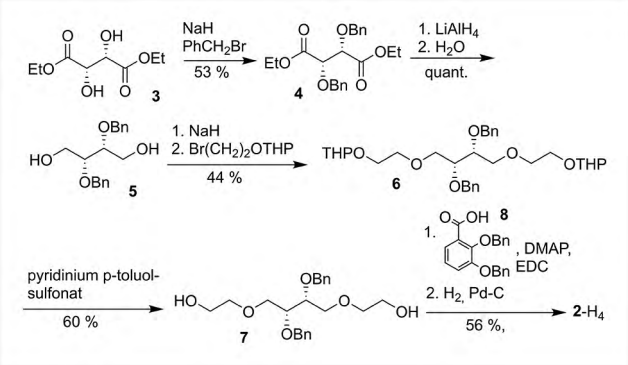


Figure 1 Biscatechol ligands for the stereoselective self-assembly of expandable and compressible helicates.

Results and Discussion

The preparation of ligand **2**-H_4 follows the sequence shown in Scheme 1. The tartaric acid ester **3** is benzyl-protected to obtain **4**, which is reduced with $LiAlH_4$ to obtain diol **5**. This is elongated to the benzyl-protected **6**. Removal of the THP groups affords again a diol **7**, which finally is coupled with the benzyl-protected catechol **8** to afford, after removal of the protecting groups, the ligand **2**-H_4.

In a coordination study, ligand **2**-H_4 (3 equiv.) and TiO $(acac)_2$ (2 equiv.) are reacted in methanol in the presence of appropriate bases (2 equiv., M_2CO_3, M = Li, Na, K).[4] For the



Scheme 1 Preparation of ligand **2**-H_4.

lithium salt $Li_4[Ti_2\mathbf{2}_3]$, a well-resolved NMR spectrum is observed in DMSO-d_6. The ESI MS reveals in the negative mode the signals of the monoanionic helicate at $m/z = 1551.2829$ (calcd. $m/z = 1551.2778$).[5] The corresponding sodium or potassium salts, $M_4[Ti_2\mathbf{2}_3]$, show rather broad signals by NMR as observed in earlier cases, but they again show in the ESI MS the presence of helicate-type complexes $M_3[Ti_2\mathbf{2}_3]^-$ (M = Na: 1599.1966, calcd.: 1599.1991; M = K: 1647.1262, calcd. 1647.1209). The different spectroscopic behavior already shows the difference of the compressed lithium compound in comparison to the expanded sodium and potassium salts (Figure 2).

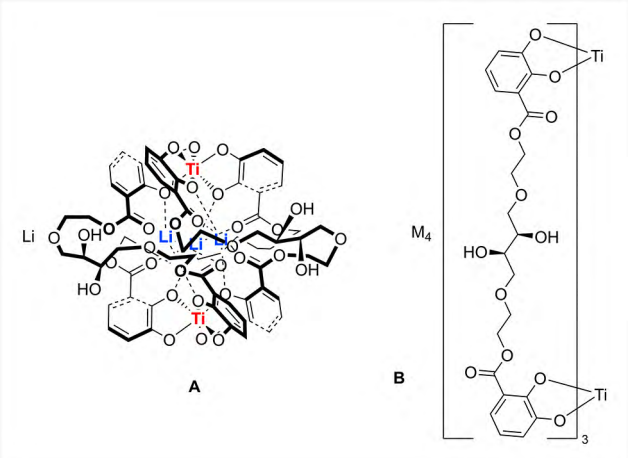


Figure 2 The compressed complex $Li_4[Ti_2\mathbf{2}_3]$ (A) and the expanded helicate-type complexes $M_4[Ti_2\mathbf{2}_3]$ (B, M = Na, K).

The lithium salt $KLi_3[Ti_2\mathbf{2}_3]$ was crystallized from DMF by diffusion of diethyl ether into the solution. In order to facilitate crystallization, a trace amount of KPF_6 was added.[6]

As observed in other cases,[2] a dinuclear titanium(IV) helicate is formed, which encapsulates three lithium cations by binding to the internal ester and catechol oxygen atoms. Hereby, the three lithium atoms adopt a tetrahedral coordination geometry. The titanium ions coordinate with three catecholates, each resulting in a distorted octahedral geometry. A special feature of $Li_3[Ti_2\mathbf{2}_3]^-$ is the presence of the diol unit located in the center of the ligand spacer possessing an *SS*-configuration while the complex units show a ΔΔ configuration (right-handed twist). In $Li_3[Ti_2\mathbf{1}_3]^-$, the opposite twist (ΛΛ) was observed. In the former complex, the stereochemical control was due to the spatial requirements of the phenyl substituents close to the catecholates,[2] while in the new complex $Li_3[Ti_2\mathbf{2}_3]^-$, it was due to the position of the OH substituents in the plane of the three lithium cations ("pseudo-equatorial") (Figure 3).

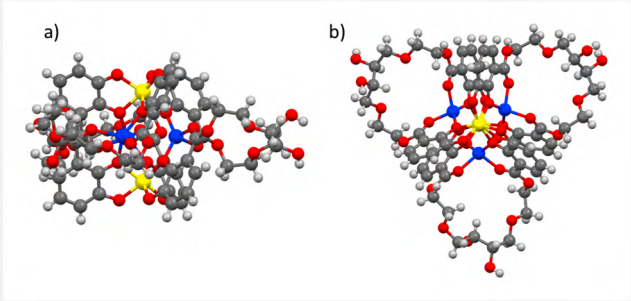


Figure 3 The structure of the compressed complex $Li_3[Ti_2\mathbf{2}_3]^-$ in the crystal. a) Side view, b) top view; grey: C, white: H, blue: Li, red: O, yellow: Ti.

Upon addition of [2.1.1]cryptand to the complex $Li_4[Ti_2\mathbf{2}_3]$, lithium cations are removed, switching the structure to its expanded form. Addition of LiCl reverses this process. This can be nicely observed by following the NMR signals of the catecholate units (Figure 4).

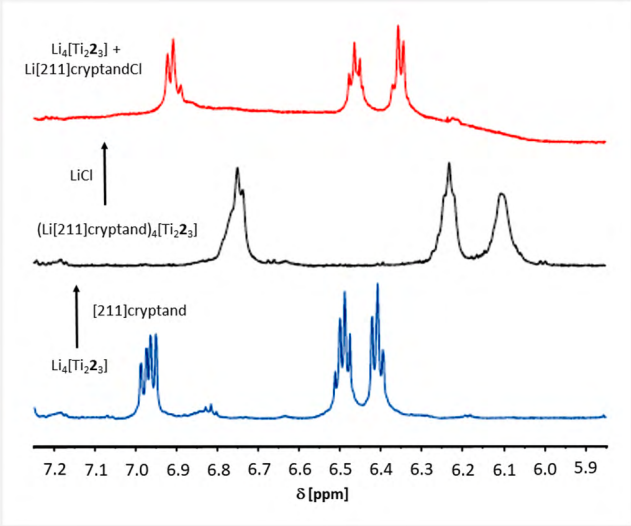


Figure 4 Expansion and compression of the helicate by removing and addition of lithium cations.

In order to evaluate the stereochemistry of the compressed and expanded helicate in solution, CD spectra of the complex $Li_4[Ti_2\mathbf{2}_3]$ were measured (Figure 5). The observed Cotton effects between 300 and 500 nm represent the chirality of the titanium catecholates. Hereby, the ΔΔ configuration is confirmed for the metal complex units in solution (blue line) as has been found by X-ray diffraction.[7] Upon addition of [2.1.1]-cryptand, the chiral induction of the diol on the complex units nearly vanishes (black line) but is in part recovered upon addition of LiCl (red line). The sodium and potassium salts $M_4[Ti_2\mathbf{2}_3]$ (M = Na, K) show CD spectra similar to the lithium compound with much lower intensity of the Cotton effects. This indicates a less effective induction of the stereochemistry at the complex units and explains the observation of broad signals by NMR spectroscopy.

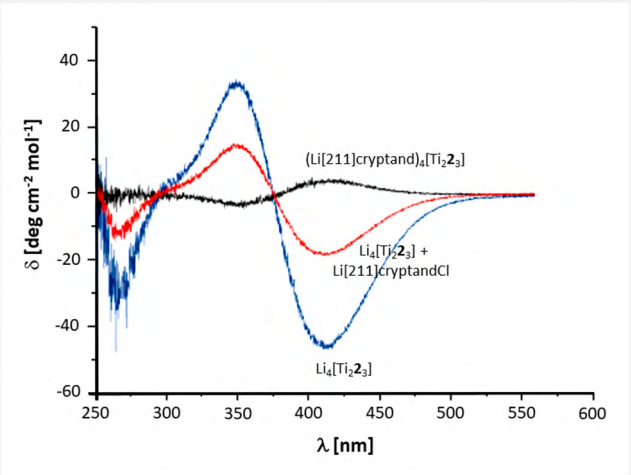


Figure 5 CD spectra of $Li_4[Ti_2\mathbf{2}_3]$ upon successive addition of [2.1.1]-cryptand and LiCl in DMSO solution. The CD spectrum after successive addition of cryptand and LiCl does not correspond to the initial spectrum due to the addition of cryptand and LiCl dissolved in DMSO.

Conclusions

In here we presented a new length-switchable helicate with central diol units in the spacer. The chirality of the spacer is transferred to the metal complex units and in the expanded form of the helicate it strongly controls the helicity of the complex. This stereocontrol is lost upon expansion.

The introduction of the diol unit at the ligand enables further reactivity of the helicate, e.g., for metal coordination or for the generation of switchable catalysts.[8]

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Supporting Information

Supporting Information for this article is available online at https://doi.org/10.1055/a-1945-0582.

Conflict of Interest

The authors declare no conflict of interest.

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(5) Ligand **2**-H_4 (28.2 mg, 0.058 mmol, 3.0 equiv.) was dissolved in dichloromethane (30 mL). After adding titanium (IV) oxybisacetylacetonate (10.2 mg, 0.039 mmol, 2.0 equiv.) and lithium carbonate (2.9 mg, 0.039 mmol, 2.0 equiv.), the reaction mixture was stirred for 24 h. Upon completion, the solvent was evaporated to afford $Li_4[(\mathbf{2})_3Ti_2]$ (yield = quant.) as a red solid. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.97 (m, 5 H), 6.50 (m, 6 H), 6.41 (m, 6 H), 4.18 (m, 6 H), 4.09 (t, J = 11.1 Hz, 3 H), 3.95 (t, J = 10.7 Hz, 4 H), 3.24–3.20 (m, 9 H), 3.17 (m, 6 H), 3.08 (t, J = 6.4 Hz, 3 H), 3.01 (d, J = 6.0 Hz, 3 H), 2.94 (d, J = 12.3 Hz, 4 H), 2.89 (d, J = 12.0 Hz, 4 H) ppm. Signals not listed are overlapping and cannot be assigned. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3369, 2923, 2862, 2451, 2290, 2207, 2157, 2076, 1923, 1676, 1593, 1561, 1444, 1373, 1294, 1252, 1213, 1129, 1064, 1037, 984, 801, 743, 681. ESI-MS: *m/z*: calculated for $C_{66}H_{66}Li_3O_{66}Ti_2^-$ ([M – Li]$^-$): 1551.2778; found: 1551.2829. Elemental analysis: calculated for $C_{66}H_{66}Li_4O_{66}Ti_2$: C: 50.86%, H: 4.27%; found: C: 48.93%, H: 4.96%.

(6) Single-crystal X-ray data were measured using a Rigaku SuperNova dual-source Oxford diffractometer equipped with an Atlas detector using mirror-monochromated Cu-*K*α (λ = 1.54184 Å) radiation. The data collection and reduction were performed using the program *CrysAlisPro* (Rigaku Oxford Diffraction, 2018, *CrysAlisPro*, Rigaku Corporation, Oxford, UK) and an empirical absorption correction method using spherical harmonics correction was applied. The structure was solved with intrinsic phasing (*ShelXT*) (Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2015**, *71*, 3) and refined by full-matrix least squares on F^2 using the *Olex2* software (Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.*, **2009**, *42*, 339), which utilises the *ShelXL*-2015 module (Sheldrick, G. M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2015**, *71*, 3). Anisotropic displacement parameters were assigned to non-H atoms. All hydrogen atoms were refined using riding models with U_{eq}(H) of 1.5 U_{eq}(C/O) for methyl/hydroxyl groups and U_{eq}(H) of 1.2 U_{eq}(C) for all other C – H groups (methylene, aromatic). Crystal data for $KLi_3[\mathbf{2}_3Ti_2]$: $C_{16}H_{13}FN_2O$, M = 1956.38, orange needle, 0.03 × 0.06 × 0.16 mm³, monoclinic, space group $P2_1$, a = 16.9444(2) Å, b = 18.6694(2) Å, c = 18.0956(3) Å, β = 96.342(1)°, V = 5689.36(13) Å³, Z = 2, D_{calc} = 1.142 gcm⁻³, F000 = 2044, μ = 2.18 mm⁻¹, T = 120.0(1) K, θ_{max} = 76.2°, 22155 total reflections, 19518 with $I_o > 2\sigma(I_o)$, R_{int} = 0.035, 22155 data, 1257 parameters, 87 restraints, GooF = 0.99, $R_1[I_o > 2\sigma(I_o)]$ = 0.042 and wR_2 = 0.105, 0.27 < $d\Delta\rho$ < −0.26 eÅ⁻³, Flack = 0.018(5), CCDC-2180683.

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