Letter

Self-assembly of a triple-stranded helicate from a rigid di(catechol) ligand and formation of its dimer in the solid state

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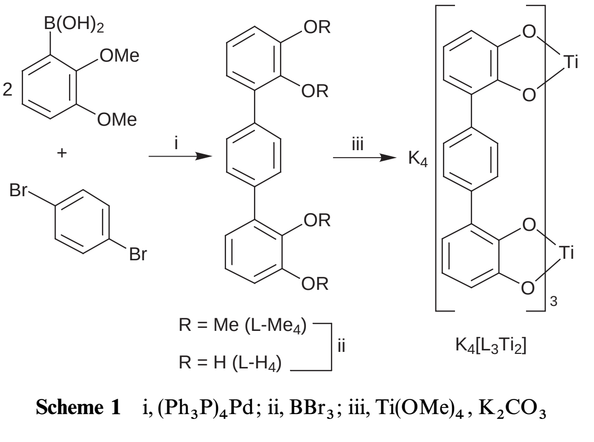
The *p*-phenylene bridged di(catechol) ligand L-H_4 forms a triple-stranded dinuclear titanium helicate which in the solid state incorporates potassium cations and forms a dimeric species.

Triple-stranded helicates are formed by self-assembly processes from two (or more) metal ions that prefer an octahedral coordination environment and three linear ligands with two (or more) bidentate ligand units.[1] Recently we described the self-assembly of cryptand-type helicates and meso-helicates from alkyl-bridged di- and tri-(catechol) ligands and titanium(IV) ions. Owing to the flexibility of the spacer, the cavity of the metalla-cryptand can adopt different sizes and thus shows only low selectivity towards binding of different cations.[2] In this paper we describe a rigid *p*-phenylene bridged di(catechol) ligand L-H_4, which is used for the formation of dinuclear helicate-type complexes with a defined cavity size.

A rigid di(bipyridine) ligand has already been used by Lehn and co-workers for the formation of a double stranded helicate,[3] and Raymond and co-workers described the triple-stranded helicate of a rigid *p*-phenylene bridged di(catechol) which additionally bears two amide linkages in the spacer. The amide groups allow some flexibility of the system and prevent the binding of counter ions in the interior of the helicate.[4]

The ligand L-H_4 was synthesized by Suzuki coupling of 2,3-dimethoxyphenylboronic acid[5] (2 equiv.) with 1,4-dibromobenzene (1 equiv.) followed by cleavage of the methyl ethers with BBr_3. The coordination compound $K_4[L_3Ti_2]$ was prepared by dissolving L-H_4 (3 equiv.), $Ti(OMe)_4$ (2 equiv.) and K_2CO_3 (2 equiv.) in methanol. Overnight a red solution was formed. Solvent was evaporated and the residue was dried in vacuum. The ^1H NMR spectrum (methanol-d_4) of the red compound has signals at $\delta = 6.61$ (dd, $J = 1.4$, 7.7 Hz, 6 H), 6.50 (pseudo t, $J = 7.7$ Hz, 6 H), and 6.41 (dd, $J = 1.4$, 7.7 Hz, 6 H) for the ligand units and a singlet at $\delta = 7.60$ (12 H) for the three spacer *p*-phenylene groups. Corresponding ^{13}C NMR signals (methanol-d_4) are observed at $\delta = 160.7$ (C), 158.3 (C), 139.3 (C), 129.7 (CH), 125.5 (C), 118.5 (CH), 118.1 (CH), and 111.6 (CH). However, the structure of the complex (*e.g.*, helicate *versus* meso-helicate) can not be assigned by spectroscopic methods in solution. Therefore we crystallized $K_4[L_3Ti_2]$ from dmf–ether to obtain red crystals of composition $K_4[L_3Ti_2] \cdot 8$ dmf $\cdot H_2O \cdot 0.5$ methanol which could be investigated by X-ray crystallography.†



Scheme 1 i, $(Ph_3P)_4Pd$; ii, BBr_3; iii, $Ti(OMe)_4$, K_2CO_3

In the solid state the tetraanion $[L_3Ti_2]^{4-}$ [Fig. 1(*a*)] adopts a helical structure with a Ti—Ti separation of 8.404 Å. The rigidity of the ligand L allows no strong turn of the helicate. Thus, the estimated pitch of the helix is *ca.* 21 nm.[1] Owing to different orientations of the *p*-phenylene units of the spacers the complex does not possess C_3-symmetry in the crystal. The three ligands L and two titanium(IV) ions form a twisted cylinder with a large cavity in its interior. Some of the counter ions are located within this cylinder and these additionally bind to dmf or water molecules. Two dinuclear complexes $[L_3Ti_2]^{4-}$ which possess opposite helicity form a dimer in the solid state [Fig. 1(*b*), Fig. 2]. Just recently the formation of a meso-helicate by dimerization of two oppositely configurated dinuclear helicates in the solid state was observed by Constable *et al.*[6] Two potassium cations are bound in the interior of each of the helicates.[7] One of the cations (four-coordinate) coordinates to an internal oxygen atom of one ligand, L, and additionally is bound to two dmf molecules and one water. The water probably is fixed by hydrogen bonding

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† X-Ray crystal structure analysis of $K_4[L_3Ti_2] \cdot 8$ dmf $\cdot$ water $\cdot$ 0.5 methanol. Formula $C_{54}H_{30}K_4O_{12}Ti_2 \cdot 8\ C_3H_7NO \cdot H_2O \cdot 0.5\ CH_3OH$, $M = 1741.79$, $0.25 \times 0.20 \times 0.10$ mm, $a = 13.124(1)$, $b = 14.790(2)$, $c = 23.042(6)$ Å, $\alpha = 85.68(2)$, $\beta = 81.42(1)$, $\gamma = 73.21(1)°$, $V = 4231.5(13)$ Å^3, $\rho_{calc.} = 1.367$ g cm^{-3}, $\mu = 4.60$ cm^{-1}, empirical absorption correction *via* φ scan data ($0.986 \leqslant C \leqslant 0.999$), $Z = 2$, triclinic, space group $P\bar{1}$, (No. 2), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 11 619 reflections collected ($\pm h$, $+k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.54$ Å^{-1}, 11 037 independent and 4205 observed reflections [$I \geqslant 2\ \sigma(I)$], 1022 refined parameters, $R = 0.070$, $wR^2 = 0.158$, max. residual electron density 0.79 (-0.75) e Å^{-3}, hydrogens are calculated and refined as riding atoms, O141 to C145 refined with common U_{iso}, O71 to C75 taken as a model for SAME, S.O.F. for O161 and C162 0.5, group not refined, hydrogen atoms at O151 not found.

Data set was collected with an Enraf-Nonius MACH3 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-97, structure refinement SHELXL-97, graphics SCHAKAL-92. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 44/041.

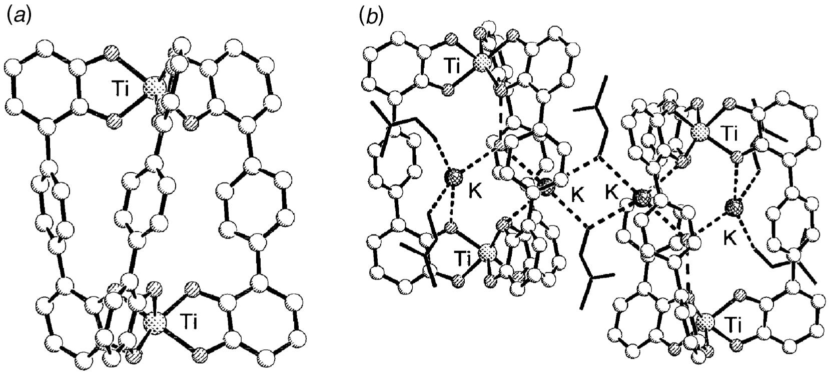

Fig. 1 Molecular structure of the helicate $\{L_3Ti_2\}^{4-}$ (*a*) and of the dimer $[\{L_3Ti_2\}K_2(dmf)_3(H_2O)]^{4-}$ (*b*) in the solid state (hydrogens are omitted)

to two internal oxygen atoms of the titana-cryptand and bridges to the second potassium ion which is coordinated to two ligand oxygen atoms. This five-coordinated potassium ion forms a four-membered ring with a symmetry equivalent potassium cation by two bridging dmf molecules. Thus a dimer is formed in the solid state. Additionally, four potassium cations (not shown) are exohedrally bound to the helicate and are saturated by further dmf molecules.

In this paper we presented the self-assembly of a cylindrical cryptand-type helicate from a *p*-phenylene bridged di(catechol) ligand and titanium(IV) ions. The tetraanion $[L_3Ti_2]^{4-}$ possesses a well-defined cavity size in which potassium cations can be incorporated; in the solid state the potassium ions form a dimer with dmf bridges. At the moment we are preparing further rigid di(catechol) ligands to vary the size of the cavities of the self-assembled dinuclear coordination compounds.

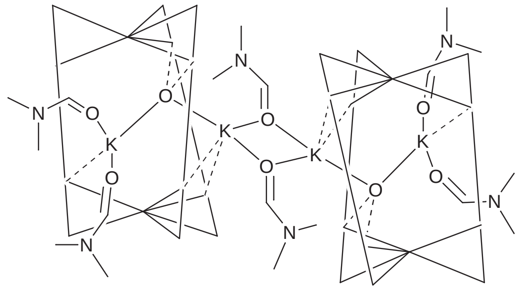

Fig. 2 Schematic representation of the dimer $[\{L_3Ti_2\}K_2(dmf)_3(H_2O)]^{4-}$ as found in the solid state. The two dinuclear helicates $\{L_3Ti_2\}^{4-}$ only are indicated

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References

1 C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; M. Albrecht, *Chem. Soc. Rev.*, in the press.
2 M. Albrecht and S. Kotila, *Angew. Chem.*, 1995, **107**, 2285; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2134; M. Albrecht and S. Kotila, *Angew. Chem.*, 1996, **108**, 1299; *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1208; M. Albrecht and M. Schneider, *Chem., Commun.*, 1998, 137.
3 P. N. W. Baxter, J.-M. Lehn and K. Rissanen, *Chem. Commun.*, 1997, 1323.
4 B. Kersting, M. Meyer, R. E. Powers and K. N. Raymond, *J. Am. Chem. Soc.*, 1996, **118**, 7221; M. Meyer, B. Kersting, R. E. Powers and K. N. Raymond, *Inorg. Chem.*, 1997, **36**, 5179.
5 I. Prévot-Halter, T. J. Smith and J. Weiss, *J. Org. Chem.*, 1997, **62**, 2186.
6 E. C. Constable, M. Neuburger, L. A. Whall and M. Zehnder, *New J. Chem.*, 1998, **22**, 219.
7 See for comparison: M. Albrecht, H. Röttele and P. Burger, *Chem. Eur. J.*, 1996, **2**, 1264.

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