Counter-ion induced self-assembly of a *meso*-helicate type molecular box

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The self-assembly process of binuclear *meso*-helicate type coordination compounds from three CH_2-bridged bis(catechol) ligands (H_4L) and two titanium(IV) ions is induced by Li^+ or Na^+ but not by K^+; in the solid state $Li_3[L_3Ti_2]^-$ forms a molecular box.

Metallo-supramolecular architectures can be formed in spontaneous self-assembly processes from metal ions and organic components (ligands).[1] The self-assembly can be supported by the templating ability of one (or more) of the components.[2] For example the tetraplex formation of guanine bases is induced by main-group metal ions (*e.g.* Na^+).[3]

Recently, we described the stereoselective self-assembly of anionic helicate and *meso*-helicate type coordination compounds which in the solid state, as well as in solution, are able to incorporate alkali-metal cations.[4] The cations are a part of the molecular structure and thus should play an active part in the self-assembly process. Herein we describe the sodium or lithium induced self-assembly of a methylene bridged binuclear titanium(IV) *meso*-helicate. Reaction of bis(2,3-dihydroxyphenyl)methane (H_4L, 3 equiv.)[5] with $[TiO(acac)_2]$ (acac = acetylacetonate, 2 equiv.) and K_2CO_3 (2 equiv.) affords a red soluble solid of the composition '$K_4[(L)_3Ti_2]\cdot 8H_2O$' (elemental analysis) which shows typical UV–VIS absorptions for tris(catecholate) titanium(IV) compounds and a peak in the FAB(−) MS (glycerin) at *m/z* 897 ($K_3[L_3Ti_2]^-$, low intensity). However, ^1H NMR spectroscopy reveals that no defined product is formed (Fig. 1).

If the same reaction is performed in the presence of Na_2CO_3 or Li_2CO_3 it leads to well defined products.† In the ^1H NMR spectrum in CD_3OD $Na_4[L_3Ti_2]$ displays one set of signals for the protons of the aromatic moiety at δ 6.74 (d, *J* 7.7 Hz), 6.53 (t, *J* 7.7 Hz), 6.29 (d, *J* 7.7 Hz), 3.73 (d, *J* 13.5 Hz) and 3.19 (d, *J* 13.5 Hz). The diastereotopic behaviour of the methylene protons clearly reveals that the binuclear metal complex adopts the achiral *meso*-helicate type structure ($\Lambda\Delta$). For $Li_4[L_3Ti_2]$ a similar set of signals can be observed (Fig. 1).

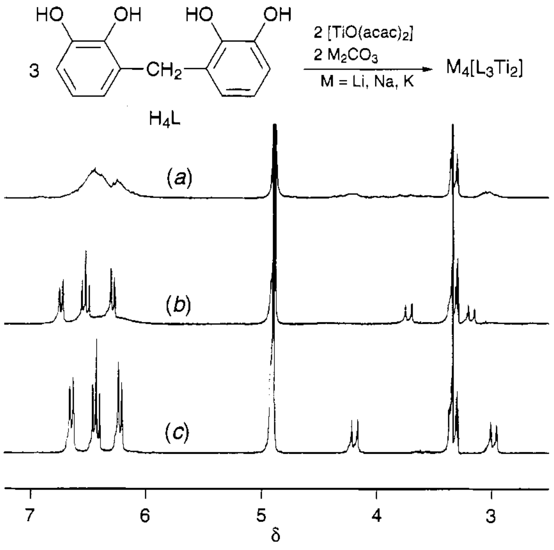

Fig. 1 ^1H NMR spectra of $M_4[L_3Ti_2]$ in CD_3OD (250 MHz); (*a*) M = K, (*b*) M = Na, (*c*) M = Li

The templating ability of the Li^+ or Na^+ ions was further tested by addition of $LiClO_4$ or $NaClO_4$ (4 equiv.) to a solution of '$K_4[L_3Ti_2]\cdot 8H_2O$' in CD_3OD. After 1 h signals of defined species can be observed and within 20 h only resonances of the binuclear titanium(IV) *meso*-helicates can be detected by ^1H NMR.

In the solid state $Li_4[L_3Ti_2]\cdot 6dmf$‡ possesses two typical titanium(IV) tris(catecholate) units (Fig. 2).[6] The complex moieties are connected by three methylene bridges to form a *meso*-helicate type structure. Thus, $[L_3Ti_2]^{4-}$ shows the same $\Lambda\Delta$ configuration in the solid state as observed in solution.[7]

The tetraanion $[L_3Ti_2]^{4-}$ forms a cavity with the six internal oxygen atoms positioned in a trigonal-prismatic arrangement (O···O 2.63–2.86 Å). The cavity should ideally fit for the uptake of alkali-metal cations. For example, an encapsulated lithium cation would have six favourable Li–O contacts of *ca.* 2.0 Å. However, *no* Li^+ can be observed in the interior of the cryptand-type anion. Three of the cations are capping the squares of the trigonal prism formed by oxygen atoms thus blocking the 'entrances' of the anion cavity and forming an empty molecular box. The three Li^+ are additionally bound to dmf molecules showing a pseudo-square-pyramidal coordination geometry. The fourth lithium atom is located in a solvent matrix (three dmf) and forms a dimer $[Li_2(dmf)_6]^{2+}$ with another symmetry related lithium atom. In summary, we could show that the self-assembly of oligonuclear coordination compounds highly depends on the nature of the counter ion. The stabilization of the thermodynamically most favoured aggregates by cation coordination is important for the selective formation of defined supramolecular species like *e.g.* molecular boxes.[8]

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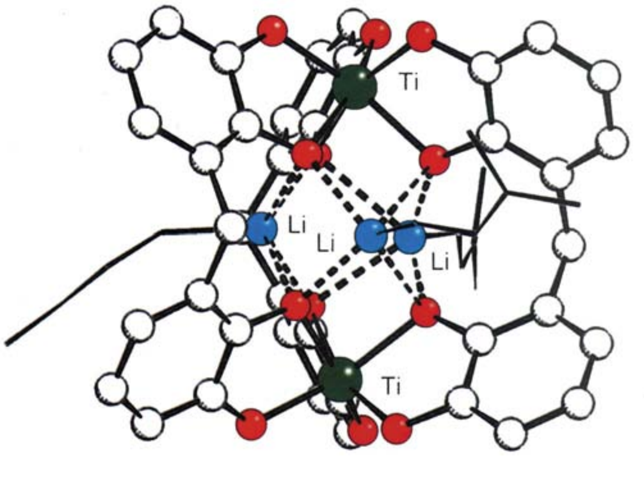

Fig. 2 Molecular structure (SCHAKAL) of the $[Li_3[L_3Ti_2]\cdot 3dmf]^-$ anion in the crystal (hydrogens are omitted for clarity; dmf molecules are only indicated); O (red), Li (blue), Ti (green)

Footnotes

† The compounds $M_4[L_3Ti_2]$ (M = Li, Na) have been characterized by elemental analyses, ^1H, ^{13}C NMR, FAB(−)-MS, and UV–VIS spectroscopy.

‡ *Crystal data* for $Li_4[L_3Ti_2]\cdot 6dmf$: $C_{57}H_{66}Li_4N_6O_{18}Ti_2$, M = 1246.72, triclinic, space group $P\bar{1}$, red crystals, a = 12.524(2), b = 12.562(1), c = 22.425(2) Å, α = 75.97(1), β = 73.91(1), γ = 61.63(1)°, U = 2957.0(6) Å^3, Z = 2, D_c = 1.400 g cm^{-3}, T = −100 °C, R = 0.037, wR_2 = 0.116, GOF = 1.081 for 911 parameters and 9644 observed reflections out of 11966 unique. Non-hydrogen atoms were refined anisotropically, hydrogens were introduced at their idealized positions and refined as riding atoms. Three dmf molecules out of six were disordered and they were refined using thermal and geometrical restraints. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/202.

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