Racemisation behaviour of trinuclear helicates formed from ethylene-bridged tris(catechol) ligands and titanium(IV) ions

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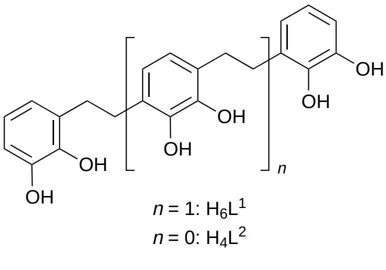
Trinuclear helicates are self-assembled from ligand H_6L^1 and Ti^{IV} ions in the presence of sodium or potassium carbonate and they racemise by consecutive inversion of the three complex units.

Movement, flexibility and dynamic behaviour are important features of chemical compounds. Although we tend to rationalise and visualise molecules as rigid structures, their behaviour very often is dominated by their ability to move or to undergo conformational changes. A very simple dynamic process of a supramolecular aggregate which is formed in a metal-directed self-assembly process is the racemisation of helicates.[1–3] In some special cases this process can be followed by NMR spectroscopy using diastereotopic protons as a stereochemical probe.[1,2] Just recently Raymond and coworkers showed that the racemisation of dinuclear gallium helicates with bis(catecholate) ligands proceeds by stepwise inversion of the two chiral metal complex units. The energy barrier for a simultaneous inversion of the two moieties should be twice as high as those of analogous mononuclear compounds. However, very similar barriers are observed for the mono- and di-nuclear complexes.[1] Additionally we could show that the racemisation barrier of dinuclear triple-stranded cryptand-type alkyl-bridged titanium(IV) helicates depends on the length of the spacer as well as the counter-ion which is present.[2]

Herein, we present the first self-assembly of a trinuclear triple-stranded helicate, which is formed from oxygen-donor ligands.[4] Analogous trinuclear double- or triple-stranded systems which contain nitrogen donor ligands have already been described in the literature.[5] Additionally we investigated the racemisation behaviour of the coordination compounds and we can show that the racemisation of the triple-stranded helicate occurs by a stepwise inversion of the complex units.

Preparation of the coordination compounds $M_6(L^1_3Ti_3)$ (M = Na, K) is done by simple mixing of ligand H_6L^1 (1 equiv.), $TiO(acac)_2$ (1 equiv., acac = acetyl acetonate) and alkali-metal carbonate (1 equiv.) in methanol. Red solutions are formed overnight and solvent is evaporated *in vacuo*. The residue is purified by chromatography (Sephadex LH 20, methanol) to obtain red complexes $M_6(L^1_3Ti_3)$ [M = Na (20%), K (33%)].† Owing to the high charge of the complex salts, it is difficult to obtain satisfactory mass spectra. However, for $K_6(L^1_3Ti_3)$ a positive FAB MS spectrum could be obtained with glycerine as matrix showing at high molar masses only characteristic peaks at *m/z* = 1430 $[K_4(L^1_3Ti_3H_3)^+]$, 1469 $[K_5(L^1_3Ti_3H_2)^+]$ and 1507 $[K_6(L^1_3Ti_3H)^+]$.



The ^1H NMR spectra (CD_3OD, 500 MHz) of the sodium *cf.* the potassium salt possess different features. NMR signals of the sodium salt $Na_6(L^1_3Ti_3)$ are observed at δ = 6.42 (dd, *J* 7.6, 1.6 Hz, 6 H), 6.36 (s, 6 H), 6.36 (t, *J* 7.6 Hz, 6 H) and 6.25 (dd,

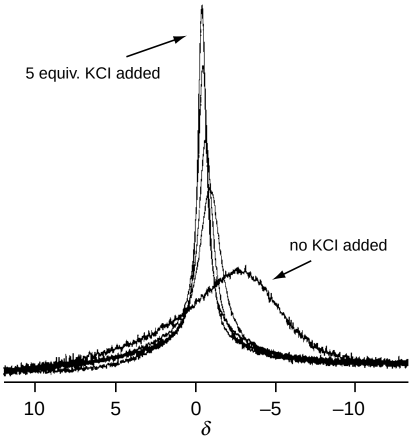


Fig. 1 Change of the ^{23}Na NMR signal of $Na_6(L^1_3Ti_3)$ in $D_2O–H_2O$ upon addition of KCl

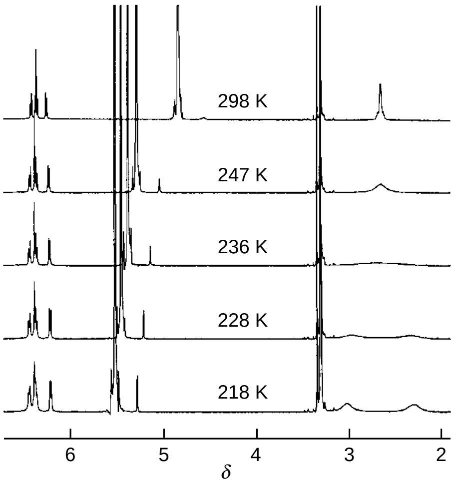
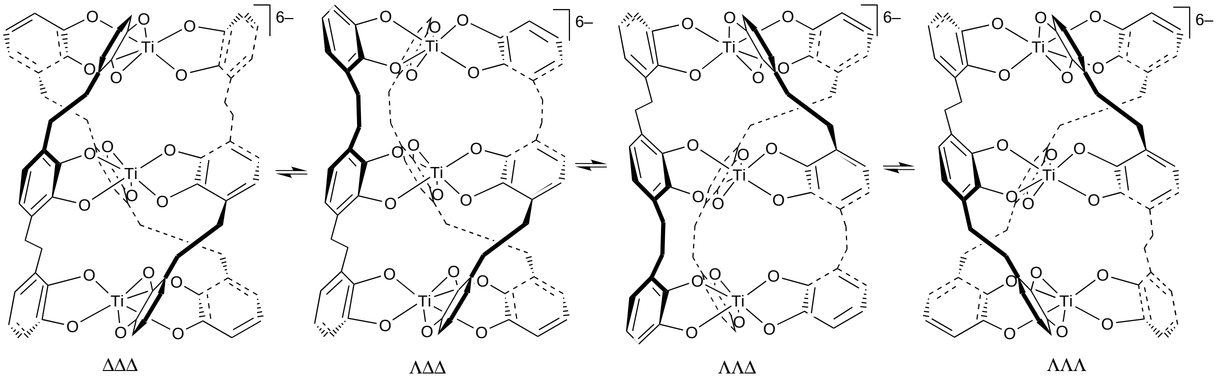


Fig. 2 ^1H NMR spectra of $Na_6(L^1_3Ti_3)$ at variable temperature (CD_3OD)

Table 1 Free energy barriers ($\Delta G^\ddagger$) for the racemisation of di- and trinuclear helicates $M_4(L^2_3Ti_2)$ and $M_6(L^1_3Ti_3)$ (M = Na, K

	$\Delta G^\ddagger$/kJ mol^{-1}	
	M = Na (CD_3OD)	M = K (D_2O)
$M_6(L^1_3Ti_3)$	43.9	70.7
$M_4(L^2_3Ti_2)^a$	45.2	64.4
$\Delta G^\ddagger_{tri}/\Delta G^\ddagger_{di}$	0.97	1.10

[a] Ref. 2.



Scheme 1 Mechanism of the stepwise racemisation of ΔΔΔ-$[L^1{}_3Ti_3]^{6-}$ to ΛΛΛ-$[L^1{}_3Ti_3]^{6-}$

J 7.6, 1.6 Hz, 6 H) for the aromatic protons. The spacer protons lead to a multiplet at δ 2.66 (24 H). In contrast, $K_6(L^1{}_3Ti_3)$ exhibits resonances at δ 6.52 (dd, *J* 7.6, 1.2 Hz, 6 H), 6.46 (s, 6 H), 6.44 (t, *J* 7.6 Hz, 6 H) and 6.25 (dd, *J* 7.6, 1.2 Hz, 6 H) for the ligand moieties and two multiplets at δ 2.90 (m, 12 H) and 2.33 (m, 12 H) for the spacer protons. The observed NMR spectroscopic results show that for the potassium salt $K_6(L^1{}_3Ti_3)$ the racemisation of the helicate at room temp. is slow with respect to the NMR timescale while the inversion of the corresponding sodium salt is fast. This is in agreement with results obtained for the analogous dinuclear complexes $M_4(L^2{}_3Ti_2)$ (M = Na, K).[2] As we showed previously, the difference in the dynamic behaviour of different alkali-metal salts of helicates is due to inclusion of the counter-ions in the cryptand-type interior.[6]

Inclusion of counter-ions in the cavities of the trinuclear helicate $[L^1{}_3Ti_3]^{6-}$ was indicated by titration of the sodium salt with potassium chloride. ^{23}Na NMR spectroscopy [D_2O–H_2O (1 : 1), 105.8 MHz, Fig. 1)] at room temp. shows that the initial broad signal at δ −2.4 ($\Delta\nu_{\frac{1}{2}}$ = 625 Hz) sharpens upon addition of KCl and is shifted towards the typical resonance for solvated sodium cations at δ −0.3. This observation is due to the binding of potassium cations in the interior of the cavities and removal of sodium.[6]

Fig. 2 presents the result of a low temperature NMR spectroscopic study of $Na_6(L^1{}_3Ti_3)$ in CD_3OD (500 MHz). While cooling the NMR sample, the signal of the protons of the spacer at δ 2.66 starts to broaden and at 236 K coalescence is observed. At lower temperatures (218 K) two multiplets can be detected at δ 3.02 and 2.31 for the diastereotopic spacer protons of the chiral helicate. From those NMR spectroscopic findings a free energy barrier of $\Delta G^\ddagger$ = 43.9 kJ mol^{-1} can be estimated for the racemisation of the hexaanionic helicate with sodium counter-ions, $Na_6(L^1{}_3Ti_3)$.

Upon heating of $K_6(L^1{}_3Ti_3)$ in CD_3OD (500 MHz) coalescence can not be reached. However, if the same experiment is performed in D_2O, coalescence is observed at 364 K, indicating a racemisation barrier of $\Delta G^\ddagger$ = 70.7 kJ mol^{-1}.

As can be seen from Table 1, the observed $\Delta G^\ddagger$ values of the trinuclear complexes $M_6(L^1{}_3Ti_3)$ are very similar to those detected for the corresponding dinuclear compounds $M_4(L^2{}_3Ti_2)$. The largest deviation is found for the potassium salts with $\Delta G^\ddagger_{tri}/\Delta G^\ddagger_{di}$ = 1.1. If the racemisation proceeds by a simultaneous mechanism *via* an achiral coordination compound with three trigonal prismatic complex moieties, a ratio of $\Delta G^\ddagger_{tri}/\Delta G^\ddagger_{di}$ = 1.5 would be expected. The observed ratios of approximately 1.0 show that the racemisation takes place by a stepwise mechanism. This means that the helicate starts to invert at one terminus of the complex followed by inversion of the central complex unit and final racemisation of the second terminus (Scheme 1). (It is unlikely that the inversion starts at the central unit. This would lead to two *meso*-type relations of this unit to the two other complex moieties and would build up a high strain energy.[7])

To rule out a dissociative mechanism for the racemisation of the helicate,[1,3] NMR experiments were performed in the presence of an excess of ligand. No exchange of free and bound ligand could be observed.[6] Spin saturation transfer NMR experiments proved to be negative and thus supported our interpretations.

Using Raymond's strategy, we could show that the racemisation of flexible alkyl-bridged trinuclear tris(catecholato) titanium helicates proceeds similarly to the one of dinuclear gallium helicates with more rigid aryl amid linkages between the complex units.[1] However, in the case of $M_6(L^1{}_3Ti_3)$ the counter-ions are binding to the hexaanion and thus are influencing the racemisation barrier.

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Footnotes and References

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† $Na_6(L^1{}_3Ti_3)$: ^{13}C NMR (CD_3OD): δ 159.4 (C), 157.9 (C), 157.7 (C), 127.5 (C), 125.0 (C), 119.8 (CH), 118.7 (CH), 117.9 (CH), 110.5 (CH), 33.6 (CH_2), 33.5 (CH_2). Anal. Calc. for $C_{66}H_{48}Na_6O_{18}Ti_3\cdot 13\ H_2O$: C, 48.19; H, 4.53. Found: C, 48.33; H, 4.76%. $K_6(L^1{}_3Ti_3)$: ^{13}C NMR (CD_3OD): δ 159.0 (C), 157.5 (C, double intensity), 126.5 (C), 124.4 (C), 119.9 (CH), 119.4 (CH), 118.5 (CH), 110.1 (CH), 33.8 (CH_2), 32.5 (CH_2). Anal Calc. for $C_{66}H_{48}K_6O_{18}Ti_3\cdot 11\ H_2O$: C, 46.48; H 4.14. Found: C, 46.57; H, 4.80%.

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