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An enantiomerically pure dinuclear triple-stranded helicate: X-ray structure, CD spectroscopy and DFT calculations

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An enantiomerically pure dinuclear triple-stranded titanium(IV) helicate is formed from a dicatechol diimine ligand with an (*R*,*R*)-1,2-diaminocyclohexane spacer and its stereochemical features are elucidated by experimental and theoretical methods.

'Chirality' was an important argument in the 1874 proposals of van't Hoff[1] and LeBel[2] that tetra-substituted carbon has to adopt a tetrahedral geometry. In coordination chemistry, Werner early on proposed and later showed that octahedral metal complexes with bidentate chelating ligands are chiral.[3] Here no centre of chirality is present, as in the sense of the unsymmetrically substituted carbon atom, but the ligands adopt a helical arrangement, which has the structure of either a left handed (Λ) or a right handed (Δ) propeller.[4]

Since about one decade, we have been investigating the stereochemical features of dinuclear triple-stranded helicates, which are formed from dicatechol ligands and titanium(IV) ions.[5] Hereby we found a systematic entry to control the relative stereochemistry of the two complex units. If both possess the same configuration (ΛΛ or ΔΔ), a chiral helicate is present, while the heterochiral isomer (ΔΛ) represents an achiral meso-helicate.[6] Usually, the helicates are formed as racemic mixtures of the enantiomers, which in some cases are in equilibrium

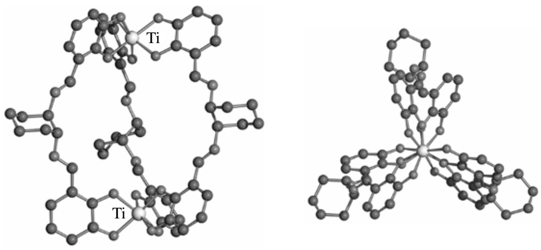


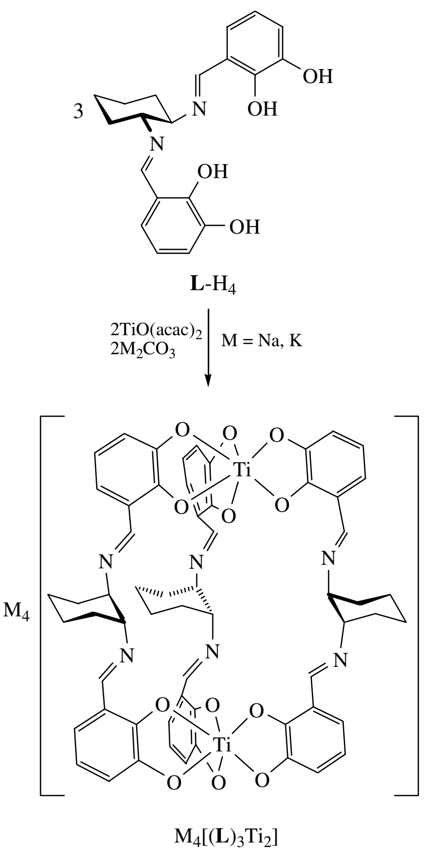
Figure 1 Solid-state structure of the tetraanion $[(\mathbf{L})_3Ti_2]^{4-}$ (left: side view, right: top view).

with each other. However, a few examples are known, where enantiomerically pure helicates are obtained by the separation of stereoisomers,[7] by induction of chirality through counterions[8] or by introduction of chiral substituents either in the spacer[9] or at the termini of the ligands.[10]

Here we present an example where we for the first time were able to obtain an X-ray structural analysis of an enantiomerically pure triple-stranded titanium(IV) helicate with dicatecholate ligands. We used our structural results and correlated them with CD-spectroscopic findings by the DFT investigation of the electronic properties of the titanium(IV) tris(catecholate) moiety.

The preparation and characterization of the dicatechol imine ligand **L**-H_4 and its complexes $M_4[(\mathbf{L})_3Ti_2]$ (M = Na, K) were described earlier.[11] Now, we were able to crystallise $K_4[(\mathbf{L})_3Ti_2]$ from DMF–diethyl ether and to obtain the solid-state structure of $K_4[(\mathbf{L})_3Ti_2]\cdot 8DMF\cdot H_2O$.

The solid-state structure of the complex is shown in Figure 1. Three ligands **L** and two titanium(IV) ions form a tetraanionic triple-stranded helicate in which the ligands wrap around the two metal centres. In order to do this, the substituents at the cyclohexane moieties have to adopt axial positions, resulting in a stretched molecule with a Ti–Ti separation of 10.263 or 10.375 Å (two independent molecules). Two of the four potassium counterions are located in the interior, each binding to two internal catecholate oxygen atoms and one DMF molecule and additional three DMF are bridging between the two cations. The remaining two potassium ions are bound to one terminus of the helicate. Those cations are bridging by solvent molecules to the next unit and form an infinite polymeric structure in the crystal.†



Scheme 1 Self-assembly of the enantiomerically pure triple-stranded helicate $M_4[(\mathbf{L})_3Ti_2]$.

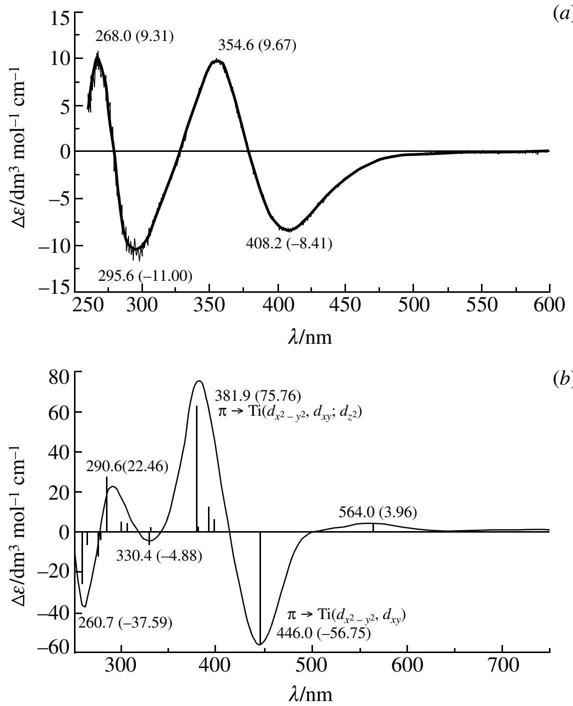


Figure 2 CD spectrum (*a*) observed for $Na_4[(\mathbf{L})_3Ti_2]$ and (*b*) calculated for $Na_2[(cat)_3Ti_2]$.

The 1,2-diaminocyclohexane units in the spacer are *R*,*R*-configurated and, therefore, chiral information is introduced, which controls the twist of the helicate. Both metal complex units adopt the Δ,Δ-configuration, so that the helicate overall possesses the structure of a right handed triple-stranded helix.

^{1}H NMR spectroscopy of the complex shows only half a set of ligand signals, which indicates configurational stability in solution. Relatively high optical rotation is observed for the complexes with $[\alpha]_D$ –489° {acetone, c = 0.069 mmol dm^{-3}, 296 K, $K_4[(\mathbf{L})_3Ti_2]$} and $[\alpha]_D$ –369° {acetone, c = 0.025 mmol dm^{-3}, 296 K, $Na_4[(\mathbf{L})_3Ti_2]$}. For comparison, ligand **L**-H_4 leads only to $[\alpha]_D$ –58.4° (acetone, c = 11.275 mmol dm^{-3}, 296 K).

$K_4[(\mathbf{L})_3Ti_2]$ is the first configurationally stable triple-stranded enantiomerically pure titanium(IV) helicate, which could be structurally characterised. Therefore, we intended to investigate the CD spectrum of the complex and, in an independent study, confirm the stereochemistry at the complex units by TDDFT calculations.

The UV-VIS spectra of the complexes $M_4[(\mathbf{L})_3Ti_2]$ in DMF are very similar showing two transitions for $K_4[(\mathbf{L})_3Ti_2]$ at 285 (ε = 53055) and 399 nm (ε = 25612), or for $Na_4[(\mathbf{L})_3Ti_2]$ at 283 (ε = 49363) and 399 nm (ε = 26663). CD spectroscopy reveals the corresponding bands for $Na_4[(\mathbf{L})_3Ti_2]$ at 268 ($\Delta\varepsilon$ = 9.31),

† *Crystal data for* $[(C_{60}H_{54}N_6O_{12}Ti_2)(C_3H_7NOK)_2(C_3H_7NO)_3]_2[(C_3H_7NO)_4K_2][(C_3H_7NO)_3H_2OK_2]C_4H_{10}O$, M = 3941.35, monoclinic, space group $P2_1$ (no. 4), a = 16.424(1), b = 27.971(1) and c = 23.581(1) Å, β = 104.63(1)°, V = 10481.8(9) Å^3, d_{calc} = 1.249 g cm^{-3}, μ = 3.81 cm^{-1}, Z = 2, λ = 0.71073 Å, T = 198 K, 75112 reflections collected (±h, ±k, ±l), $[(\sin\theta)/\lambda]$ = 0.54 Å^{-1}, 26270 independent (R_{int} = 0.067) and 18955 observed reflections [$I \geq 2\sigma(I)$], 2152 refined parameters, R = 0.085, wR_2 = 0.213. Flack parameter –0.01(3).

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 256795. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2004.

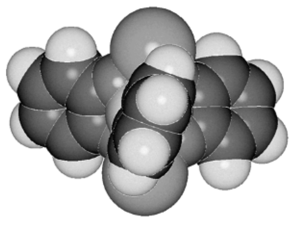


Figure 3 Structure of $Na_2[(cat)_3Ti]$ obtained by DF theory employing the B3LYP functional and a valence triple-ζ basis set augmented by polarization functions (TZVP).

295 ($\Delta\varepsilon = -11.00$), 355 ($\Delta\varepsilon = 9.67$) and 410 nm ($\Delta\varepsilon = -8.41$). The spectrum is shown in Figure 2(*a*).

While the chirality of $K_4[(\mathbf{L})_3Ti_2]$ could be determined beyond any doubt by solid-state structure analysis of suitable single crystals, no such samples could be obtained for $Na_4[(\mathbf{L})_3Ti_2]$. We, therefore, decided to determine its configuration by comparison of measured and calculated CD spectra.

The CD spectrum of $Na_4[(\mathbf{L})_3Ti_2]$ was measured in DMF ($c = 3.29\times10^{-3}$ mol dm^{-3}) at room temperature employing an AVIV 62DS spectrometer. The CD curve [Figure 2(*a*)] shows positive Cotton effects at $\lambda = 270$ and 355 nm and negative ones at $\lambda = 295$ and 410 nm.

Since the complex $Na_4[(\mathbf{L})_3Ti_2]$ is too large for a theoretical treatment at a reasonable level, we performed quantum-chemical calculations for the D_3-symmetric model compound $Na_2[(cat)_3Ti]$ where cat is the catecholate dianion ($C_6H_4O_2^{2-}$) and the two sodium cations are located on the threefold axis defined by the Ti atom and the centres of the equilateral O_3 triangles.[12] The structure of this model compound has been optimised within the framework of DF theory employing the B3LYP functional[13] and a valence triple-ζ basis set augmented by polarization functions (TZVP)[14] as implemented in the TURBOMOLE program.[15] D_3 symmetry has been imposed in the optimization process, and all calculations have been performed for the Δ isomer of the model compound. The optimised structure of $Na_2[(cat)_3Ti]$ is shown in Figure 3. The nine highest occupied and six lowest unoccupied Kohn–Sham orbitals (KSOs) are given in Figure 4.

The Ti–O distance of 1.986 Å obtained in the geometry optimization of $[(cat)_3Ti]^{2-}$ might be compared with the experimental values obtained for $K_4[(\mathbf{L})_3Ti_2]$. Ti–O bond lengths of 1.930–1.990 Å are observed (average of 1.96 Å), which correspond to those obtained by calculation. In $[Et_3NH]_2[(cat)_3Ti]$ averaged Ti–O distances of 1.966 Å are found.[12]

Using the optimised geometry, we calculated the CD spectrum of $Na_2[(cat)_3Ti]$ by time-dependent density functional theory and the origin-independent dipole velocity formalism. The calculations were performed with the same functional and basis set as in the geometry optimizations. The calculated CD curve has been obtained as a sum of Gaussians, each of which has been centred at the wavelength of the corresponding transition and multiplied with its rotational strength.[16] The empirical formula $\Gamma = k\lambda_{\mathrm{cal}}^{1.5}$ has been used to calculate the half bandwidth (Γ) of the Gaussians, where λ_{cal} is the calculated transition wavelength, and the parameter k is equal to 0.00375.[17] The resulting calculated spectrum is shown in Figure 2(*b*).

Compared with the experimental CD curve, the calculated bands are shifted by about 30 nm to the red. A very weak band calculated at about 706 nm lies outside the measured range. Moreover, its rotational strength is positive according to the dipole velocity and negative with the dipole lengths formalism, and we concluded that this band will probably be too weak to be observed under the conditions of the experiment. Another theoretically predicted Cotton effect, which has no experimental counterpart, is the one calculated at 564 nm. The corresponding rotational strength is also low compared with the values for the other bands. In addition, this band is not predicted unambiguously since in this case the dipole velocity and the dipole length formalism also give different signs. The reason for the absence of the corresponding Cotton effect from the measured spectrum might be that due to its weakness this band is buried under the relatively broad and strong negative Cotton effect with a maximum observed at 408 nm. We identify this Cotton effect with the one calculated at $\lambda = 446$ nm. This band is almost entirely due (95.1%) to a charge-transfer transition from the HOMO (Ψ_{19a_2}), which consists of the π orbitals of the $C_6H_4O_2^{2-}$ ligands, to the unoccupied orbital pair (Ψ_{34e}) above the LUMO almost entirely located at the Ti atom (d_{xy}, $d_{x^2-y^2}$). The Cotton effect calculated at 382 nm is strongly positive, and we correlate it with the one observed at 355 nm. This band is also due to charge transfer from π orbitals at the catecholate ligands (Ψ_{33e}, 55.6% and Ψ_{32e}, 38.5%) to titanium *d*-orbitals (Ψ_{34e}, $d_{xy} + d_{x^2-y^2}$ and Ψ_{22a_1}, d_{z^2}). The negative band calculated at 330 nm is assigned to the one observed at 295 nm. Here we have an almost pure (99.1%) charge transfer from ligand π orbitals Ψ_{33e} to an orbital consisting of *s* and p_z functions at the sodium atoms (Ψ_{20a_2}). Finally, we identify the positive band calculated at 291 nm with the one observed at 270 nm. Again the main contribution (70.8%) to this Cotton effect comes from a charge-transfer transition from π orbitals at the ligands (Ψ_{33e}) to titanium *d*-orbitals (Ψ_{36e}).

It might be argued that the –HC=N–C– moieties of the spacer units significantly contribute to the spectral properties of compound $Na_4[(\mathbf{L})_3Ti_2]$. We, therefore, performed additional TDDFT calculations for the CD spectrum of a model compound, where one *ortho* hydrogen atom of the cat ligands was replaced by the –HC=N–Me unit. Again the signs of the four strongest Cotton effects calculated at wavelengths > 275 nm

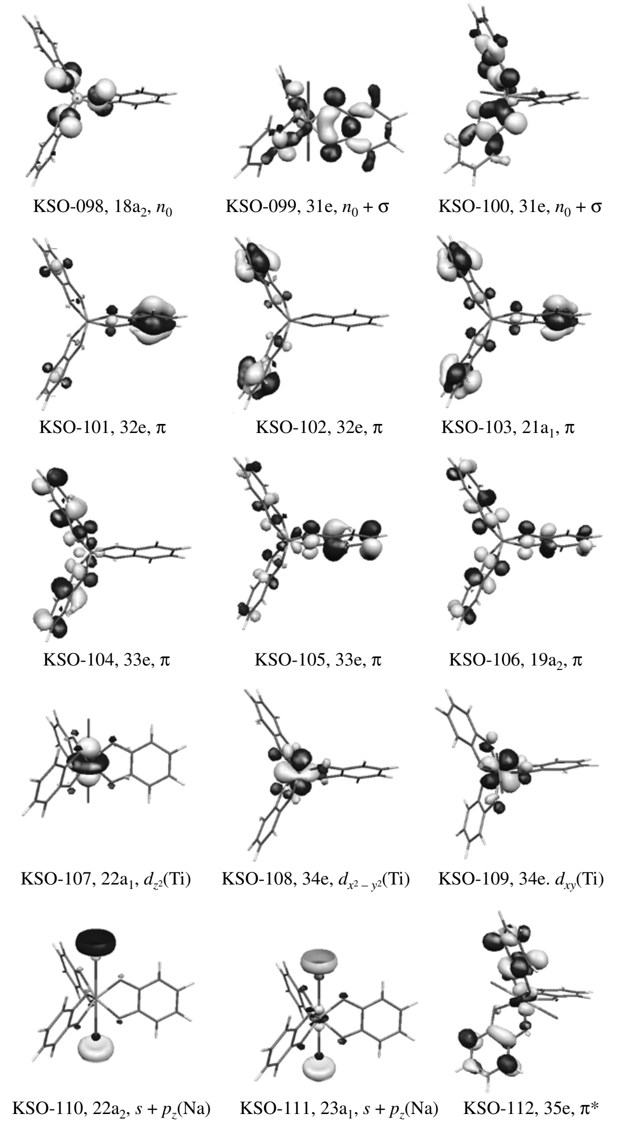


Figure 4 The nine highest occupied and six lowest unoccupied Kohn–Sham orbitals (KSOs).

agree with those in the observed spectrum, and we conclude that the –HC=N–C– units only influence the short-wavelength part of the spectrum.

Thus, the signs of all CD bands observed for $Na_4[(\mathbf{L})_3Ti_2]$ between 250 and 600 nm agree with those calculated for the Δ isomer of our model compound $Na_2[(cat)_3Ti]$ (and also for $Na_2[(cat\text{-}o\text{-}HC{=}N{-}Me)_3Ti]$). We, therefore, deduce that as was expected from the X-ray structural results for $K_4[(\mathbf{L})_3Ti_2]$ the configuration at $Na_4[(\mathbf{L})_3Ti_2]$ is also Δ.

Following the presented investigations we now have an instrument in hand to assign the stereochemistry of titanium(IV) triscatecholate complex units in metallosupramolecular aggregates with a high probability without X-ray structure analysis.

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