

Changing the Overall Shape of Heterodinuclear Helicates *via* Substitution of Acylhydrazones by Tosylhydrazones

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Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70th birthday, on recognition of his outstanding contributions to the field of metallosupramolecular chemistry

Heterodinuclear helicate-type complexes are formed from acyl and tosyl hydrazone-substituted catechol ligands. Due to the different geometry of the carboxylate compared to the sulfonate unit, different overall structures are observed for the complexes. The acylate results in the formation of a cylindrical triple-stranded system, while in the tosylate the pendant substituents fold back and form a more condensed structure.

Key words: Self-assembly, Helicates, Heteronuclear, Catechol, Hydrazone

Introduction

Metallosupramolecular chemistry opens up an easy entry to a family of complicated supramolecular architectures by simple self-assembly processes. Well-defined structures can be formed which possess special structural features as well as properties [1]. In order to introduce functionality, the concept can be used to build up heteronuclear coordination compounds with the ability for metal-metal communication. However, this requires that different metals are bound selectively at well defined positions [2].

A well investigated class of metallosupramolecular complexes are the helicates [3 – 6]. They are defined as coordination compounds in which two or more linear ligand strands are wrapped around two or more metal atoms to form a double- or triple-stranded helix [7]. A special challenge is to design ligands capable of forming sequential coordination compounds with different metal ions located in distinct positions by connecting two different ligands that are suited to coordinate different metals [8].

This concept was used by Piguet and Bünzli [9] for the formation of *d-f* heterodinuclear complexes (ligand **1**) [10] and by us for the formation of a gallium(III)-titanium(IV) complex (with ligand **2**) [11]. Recently, Hahn introduced the sequential catechol – benzenedithiol ligand **3** [12]. All the ligands **1**–**3** have the disadvantage that their preparation is cumbersome,

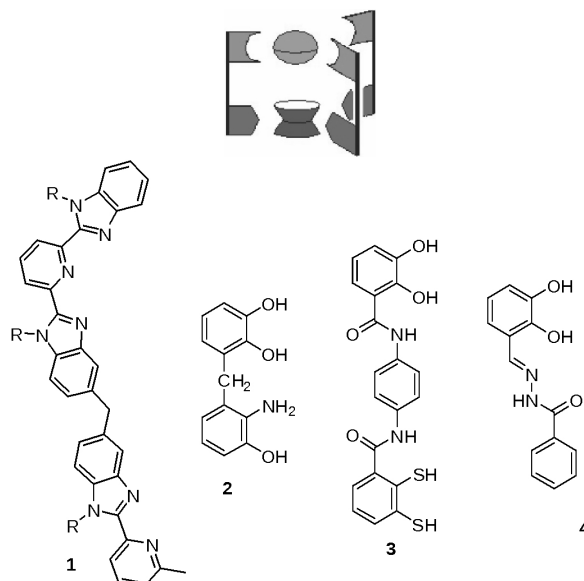


Fig. 1.

and that they are only available by multistep synthetic procedures [13, 14]. Therefore we introduced the catechol-acylhydrazone **4** (Fig. 1), which is easily available in large amounts and forms heterodinuclear helicates with gallium(III) and lanthanum(III), for example [15].

Based on these earlier results we now present the substitution of the benzoylhydrazone of **4** by tosylhy-

drazone to obtain the new ligand **5**. This changes the overall structural features of heterodinuclear coordination compounds, introducing a new arrangement of the pendant aromatic substituents relative to the heterodinuclear complex moiety.

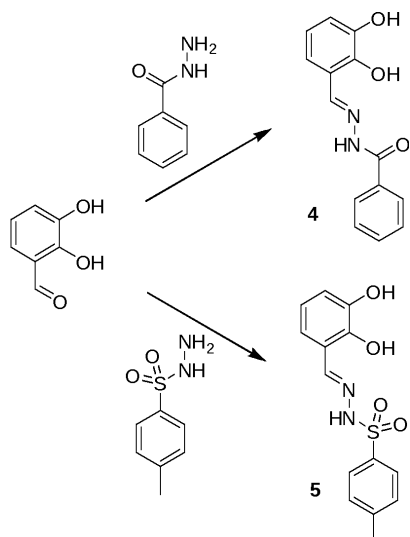
Results and Discussion

The catechol-hydrazone ligands **4** and **5**

The straightforward preparation of ligand **4** has already been described. Simple condensation of 2,3-dihydroxybenzaldehyde with benzoylhydrazone affords the ligand in high purity and very good yields [15]. By analogy, the tosylhydrazone **5** was prepared by reaction of 2,3-dihydroxybenzaldehyde with tosyl hydrazine. The desired ligand **5** was obtained in 81 % yield after recrystallization from methanol/ether (Scheme 1).

The tosylhydrazone **5** was characterized by ^1H NMR spectroscopy in $[\text{D}_4]\text{methanol}$ showing a singlet resonance for the $\text{CH}=\text{N}$ proton at $\delta = 7.96$ and two doublets at $\delta = 7.79$ and 7.39 with $J = 8.7$ Hz for the aromatic tosyl protons. The catechol hydrogen atoms lead to two resonances at $\delta = 6.82$ (1H) and 6.72 (2H). Finally, the methyl group is observed as a singlet at $\delta = 2.39$. Mass spectra and elemental analyses are also consistent with the constitution of compound **5**.

Crystals suitable for X-ray diffraction experiments were obtained for the ligand **4**. The structure shows the conformation of **4** (Fig. 2) in the solid state. A close to planar arrangement of the catechol, hydrazone and phenyl groups is observed.



Scheme 1.

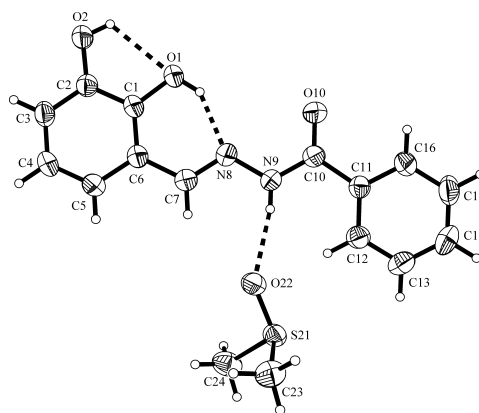


Fig. 2. Molecular structure of ligand **4**·DMSO in the solid state. The displacement ellipsoids are drawn at the 50 % probability level.

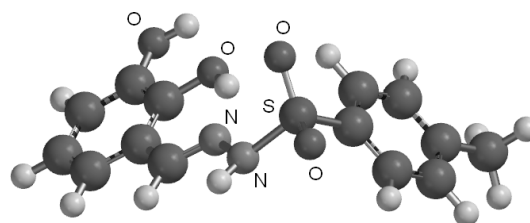


Fig. 3. Molecular structure of **5** as calculated by force field methods (SPARTAN O8).

An interesting intramolecular hydrogen bonding pattern is observed in the crystal structure of **4**. The hydroxyl group in 2-position of the catechol binds to the hydrazone =N- atom, and the OH group in 1-position is binding to the O atom in 2-position [16]. The carbonyl oxygen atom of the acyl unit is oriented to the "front" of the molecule forming the overall tridentate site for metal coordination. In addition, one molecule of DMSO cocrystallizes and becomes attached to the hydrazone hydrogen atom of **4** by intermolecular hydrogen bonding.

We were not able to obtain crystals of **5** suitable for X-ray diffraction. However, simple modeling using the force field routine of SPARTAN O8 [17] reveals the major difference between the ligands **4** and **5** (see Fig. 3) associated with the different geometries at the SO₂ unit of **5** compared to the CO unit of **4**. While the latter is planar, the sulfur atom in **5** adopts a tetrahedral coordination geometry introducing a "kink" in the ligand and leading to a non-planar structure. However, the tridentate $\text{O2}_{\text{catechol}} - \text{C}=\text{N} - \text{S}=\text{O}$ pattern for the coordination of metal ions is still intact.

Coordination studies and comparison of the structural features of complexes of ligands 4 and 5

A thorough coordination study of the ligand **4** and its bromo-substituted derivative has already been published [15]. We now report the preparation of the aluminum(III)/lanthanum(III) complex **6**, which was crystallized from DMF/methanol, and its molecular structure in the crystalline state.

With ligand **5** we tried to prepare the neutral titanium(IV)/calcium(II) complex **7b** and the cationic titanium(IV)/lanthanum(III) complex **7c**. Both coordination compounds showed the expected NMR spectra, and their ions were observed by ESI MS (**7b**: MS ((+)-ESI): $m/z = 1038.91 \{L_3TiCa+K\}^+$, MS ((-)-ESI): $m/z = 999.25 \{L_3TiCa-H\}^-$; **7c**: MS ((+)-ESI): $m/z = 2236.63 \{[L_3LaTi]_2K\}^+$ and $1123.50 \{L_3LaTiNaH\}^+$). However, no correct elemental analysis was obtained for those complexes. Finally we succeeded to obtain the anionic heterodinuclear titanium(IV)/potassium complex **7a**, which could be fully characterized. We were also able to obtain crystals of **7a** from methanol and could determine the crystal structure by X-ray diffraction (Figs. 4 and 5).

Fig. 5 shows the results of the crystallographic structure analyses of **6** and **7a** (only the triple-stranded helicate parts are shown). Fig. 5a reveals that the deprotonated ligand **4** adopts a very similar conformation in the complex **6** as was observed in the solid-state structure of the free ligand. Three of the ligands are wrapped around the two metal atoms in a helical fashion with aluminum binding to the three catechol units giving it a coordination number of six. Lanthanum(III) is coordinated to ten donor atoms with three tridentate $O_2\text{catechol} - C=N - S=O$ units of the ligands and one DMF. Fig. 5b exhibits a view down the aluminum-lanthanum axis revealing the helical arrangement of the ligands.

The related heteronuclear coordination compound **7a** adopts a very different, more compact structure. The coordination pattern again shows the helical wrapping around the metal ions. However, the tetrahedral coordination geometry around the sulfur atom introduces a break in the helical arrangement leading to a folding back of the tosyl groups into the three grooves of the triple helical complex moiety. This is nicely seen from Fig. 5c (side view) and 5d (view down the Ti–K axis).

Bond lengths between metal atoms and ligands are shorter in the aluminum/lanthanum (**6**) as compared to the titanium/potassium complex (**7a**). The Al–O

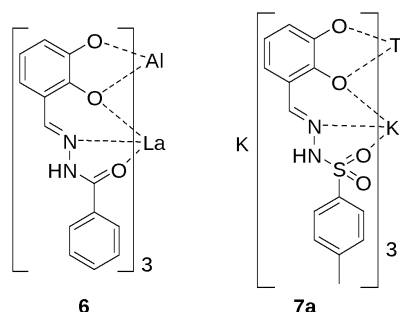


Fig. 4. The heterodinuclear helicates **6** and **7a**.

bonds to catecholate oxygen atoms are in the ranges 1.866(5)–1.881(5) (oxygen atom in 3-position) and 1.936(4)–1.956(5) Å (oxygen atom in 2-position), while corresponding titanium-oxygen separations of 1.949–19.960(5) (O3) and 1.954–1.975(5) Å (O2) are found. Hereby the bridging oxygen atoms in 2-position show longer bonds due to their lower donor character. The more highly coordinated metal atom shows its longest bond to the central nitrogen atom of the tridentate coordinating unit with the distances 2.742–2.918(6) Å for **6** and 3.065–3.191(5) Å for **7a**. Metal-to-oxygen distances are in the same range for the catecholate and the acylate or tosylate oxygen atoms with shorter bonds observed in **6** (La–O = 2.476–2.658(4) Å) in comparison to **7a** (K–O = 2.737–2.799(4) Å).

Comparison of the two structures (**6** and **7a**) reveals a very different overall geometry of the complexes. The acyl hydrazones are planar leading to a linear arrangement of the ligands and a cylinder-type structure of the dinuclear compound. In the tosyl hydrazones the folding of the ligand results in a more spherical shape of the complex. This shows that simple substitution of one connecting unit in the ligand results in differently shaped metallosupramolecular objects.

Conclusion

We have presented two ligands **4** and **5**, each having one tridentate as well as one bidentate coordination site for metal ions. Therefore they are ideal for the self-assembly of heterodinuclear helicates (**6**, **7a**) incorporating either *f*- or heavy *s*-block cations. The two ligands differ in the tridentate coordination site, with a carbonyl *versus* a sulfonyl unit. Both are able to bind to the metal cations, but result in coordination compounds with very different overall shapes. This is of course important for the development of structurally different functional derivatives based on the hetero-

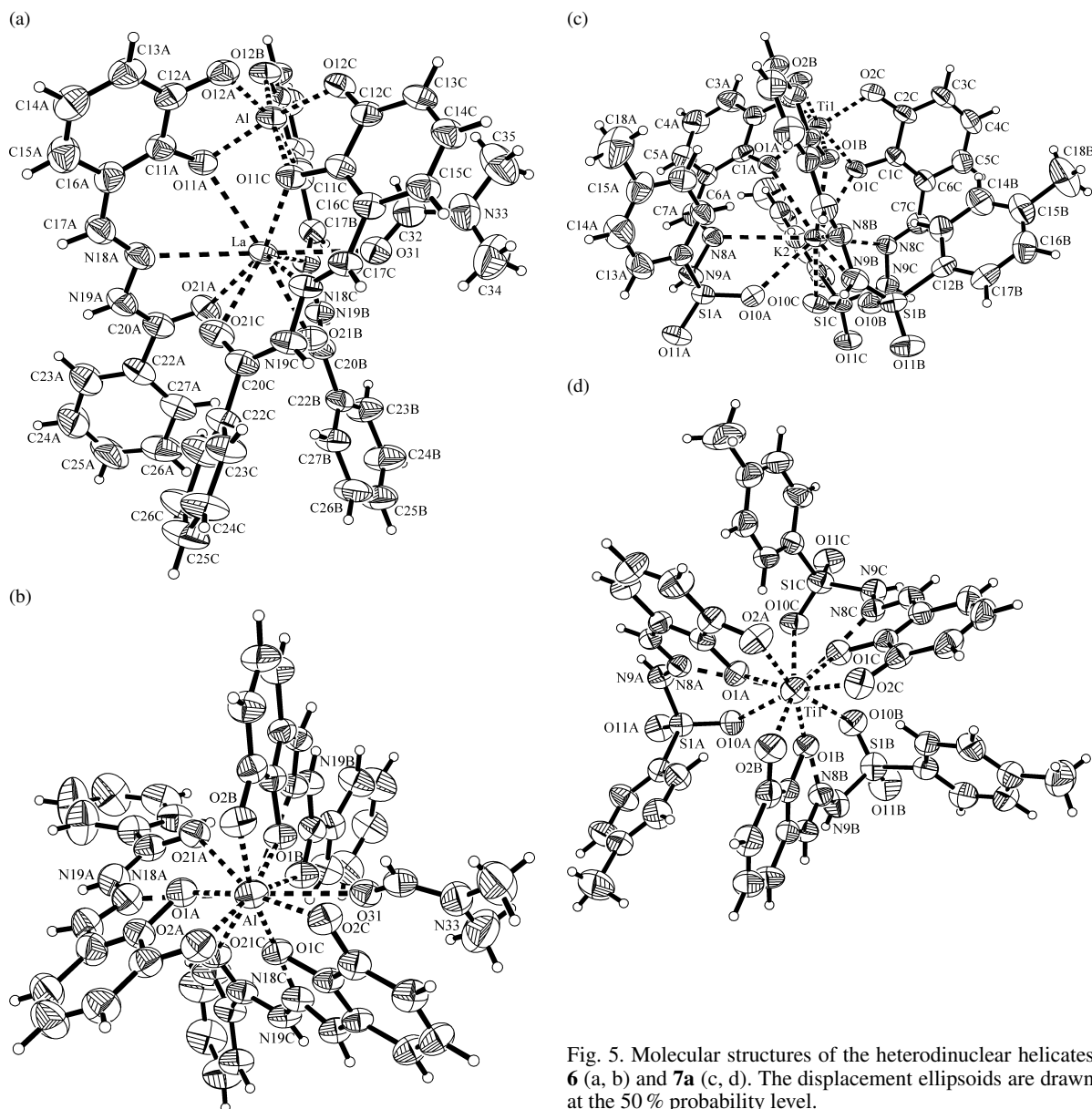


Fig. 5. Molecular structures of the heterodinuclear helicates **6** (a, b) and **7a** (c, d). The displacement ellipsoids are drawn at the 50% probability level.

dinuclear helicate core and differently arranged substituents in side chains.

Experimental Section

Commercially available reagents were used as received. The solvents were distilled and used without further purification. NMR spectra were taken on Varian Mercury 300 or Inova 400, mass spectrometric data on Finnigan SSQ 7000 and Thermo Deca XP instruments as EI (70 eV) or ESI. The infrared spectra were obtained on a PerkinElmer Spektrum

100 FTIR spectrometer and were measured in KBr ($4000 - 650 \text{ cm}^{-1}$) or neat. Elemental analyses were measured on a CHN-O-Rapid Vario EL from Heraeus, melting points on a Büchi B-540 melting point device.

Data sets were collected on a Nonius KappaCCD diffractometer with Mo radiation and equipped with a rotating anode generator. Programs used: data collection COLLECT [18], data reduction DENZO-SMN [19], absorption correction SORTAV [20,21] and DENZO [22], structure solution SHELXS-97 [23], structure refinement SHELXL-97 [24].

CCDC 755077–755079 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Ligand 4

For the preparation and characterization of **4**, see reference [15].

X-Ray crystal structure analysis of **4**: formula $C_{16}H_{18}N_2O_4S$, $M_r = 334.38$, light-yellow crystal, $0.20 \times 0.20 \times 0.05 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.9719(5)$, $b = 15.3749(7)$, $c = 9.9061(4)$ Å, $\beta = 96.670(2)^\circ$, $V = 1659.77(13) \text{ Å}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.34 \text{ g cm}^{-3}$, $\mu = 1.9 \text{ mm}^{-1}$, empirical absorption correction ($0.700 \leq T \leq 0.910$), $\lambda = 1.54178$ Å, $T = 223(2)$ K, ω and ϕ scans, 12608 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.60 \text{ Å}^{-1}$, 2947 independent ($R_{\text{int}} = 0.047$) and 2590 observed reflections [$I \geq 2 \sigma(I)$], 215 refined parameters, $R = 0.041$, $wR^2 = 0.114$, max./min. residual electron density $0.26 / -0.28 \text{ e Å}^{-3}$. Comment: Hydrogen atoms at N9 from difference fourier map, others calculated and refined as riding atoms.

Ligand 5

To a stirred solution of 4-methylbenzenesulfonylhydrazine (372.46 mg, 2 mmol, 2 equiv.) in MeOH (20 mL) at r.t. a solution of 2,3-dihydroxy-benzaldehyde (276 mg, 2 mmol, 2 equiv.) in MeOH (20 mL) was added dropwise within 4 min. The mixture was stirred for 72 h at r.t.. The solvent was removed by rotary evaporation, and the product was recrystallized twice from MeOH: Et₂O (1 : 2). Ligand **5** was obtained as a dark-grey solid (495 mg, 1.62 mmol, 81 % yield). M. p.: 187.3 °C. – ¹H NMR (400 MHz, CD₃OD): $\delta = 7.96$ (s, 1H, CH=N), 7.79 (d, $J = 8.7$ Hz, 2H, CH_{Tol}), 7.39 (d, $J = 8.7$ Hz, 2H, CH_{Tol}), 6.82 (dd, $J = 7.2$ Hz, $J = 2.5$ Hz, 1H, CH_{Cat}), 6.72 (m, 2H, CH_{Cat}), 2.39 (s, 3H, CH₃). – IR (neat): $\nu = 3485, 3218, 1615, 1593, 1475, 1367, 1318, 1281, 1200, 1159, 1062, 925, 816, 724, 663 \text{ cm}^{-1}$. – MS (EI): m/z (%) = 306.1 (100) [M]⁺. – C₁₄H₁₄N₂O₄S: calcd. C 54.89, H 4.61, N 9.14; found C 55.06 H 4.23 N 9.04.

Complex 6

100 mg of **4** (0.39 mmol, 3 equiv.), 48.4 mg of LaCl₃·7H₂O (0.13 mmol, 1 equiv.), 17.4 mg of AlCl₃ (0.13 mmol, 1 equiv.), and 54 mg of K₂CO₃ (0.39 mmol, 3 equiv.) were combined in a flask and dissolved in 10 mL of MeOH. The reaction mixture was heated to reflux for 5 min and then stirred at r.t. for 3 d. A yellow solid formed, which was filtered off and washed with Et₂O. The product was obtained as a yellow solid in 75 % yield (90 mg, 0.096 mmol). – ¹H NMR (400 MHz, [D₆]DMSO): $\delta = 8.52$ (s, 3H, CH=N), 7.77 (d, $J = 7.6$ Hz, 6H, CH_{Ph}), 7.54 (t, $J = 7.6$ Hz, 3H, CH_{Ph}), 7.24 (t, $J = 7.6$ Hz, 6H, CH_{Ph}), 6.37 (m, 9H, CH_{Cat}). – IR (neat): $\nu = 3190, 3058,$

2846, 2112, 1601, 1559, 1456, 1376, 1255, 1216, 1049, 903, 869, 759, 739, 697, 657 cm^{-1} . – MS ((–)-ESI): $m/z = 535.87$ [L₂Al][–], 927.47 [L₃LaAl–H][–]. – MS ((+)-ESI): $m/z = 929.33$ [L₃LaAlH]⁺. – C₄₂H₃₀AlLaN₆O₉·2H₂O: calcd. C 52.29, H 3.55, N 8.71; found C 51.85, H 3.46, N 8.62.

X-Ray crystal structure analysis of **6**: formula (C₁₄H₁₀N₂O₃)₃AlLa·3 C₃H₇NO·CH₃OH, $M_r = 1179.94$, yellow crystal, $0.20 \times 0.15 \times 0.10 \text{ mm}^3$, trigonal, space group $R\bar{3}$ (no. 148), $a = 41.1648(4)$, $c = 21.8016(3)$ Å, $V = 31994.2(6) \text{ Å}^3$, $Z = 18$, $\rho_{\text{calc}} = 1.10 \text{ g cm}^{-3}$, $\mu = 0.7 \text{ mm}^{-1}$, empirical absorption correction ($0.878 \leq T \leq 0.936$), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and ϕ scans, 63578 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.62 \text{ Å}^{-1}$, 14407 independent ($R_{\text{int}} = 0.076$) and 9647 observed reflections [$I \geq 2 \sigma(I)$], 645 refined parameters, $R = 0.071$, $wR^2 = 0.243$, max./min. residual electron density $1.83 / -0.83 \text{ e Å}^{-3}$.

Comment: Hydrogen atoms calculated and refined as riding atoms; solvent molecules refined with geometrical (SAME) restraints and one common isotropic thermal parameter. The structure contains voids but the contents could not be determined in a chemically meaningful way. The use of the SQUEEZE routine in PLATON did not improve the refinement.

Complex 7a

To a flask charged with a solution of 83 mg of **5** (0.27 mmol, 3 equiv.) in 10 mL of MeOH, a solution of 23.7 mg of TiO(acac)₂ (0.09 mmol, 1 equiv.) and 12.5 mg of K₂CO₃ (0.09 mmol, 1 equiv.) was added. The mixture was stirred for 72 h, then the solvent was removed under reduced pressure. The product was obtained as a dark-red solid in quantitative yield (100 mg, 0.09 mmol). – ¹H NMR (400 MHz, [D₆]DMSO): $\delta = 7.61$ (s, 3H, CH=N), 7.64 (m, 12H, CH), 6.65 (d, $J = 7.9$, 6H, CH), 6.47 (m, 6H, CH), 2.12 (s, 9H, CH₃). – IR (neat): $\nu = 3539, 3191, 3051, 2109, 1595, 1441, 1322, 1248, 1160, 1017, 921, 812, 737, 666 \text{ cm}^{-1}$. – MS ((+)-ESI): m/z (%) = 1038.93 (100) [L₃TiK₂H]⁺. – MS ((–)-ESI): $m/z = 999.00$ [L₃TiK][–]. – C₄₂H₃₆K₂N₆O₁₂S₃Ti·H₂O: calcd. C 47.72, H 3.62, N 7.95; found C 47.91, H 4.19, N 7.83.

X-Ray crystal structure analysis of **7a**: formula (C₁₄H₁₂N₂O₄S)₃K₂Ti·5 CH₃OH·H₂O, $M_r = 1217.27$, orange crystal, $0.25 \times 0.20 \times 0.10 \text{ mm}^3$, orthorhombic, space group $Pna2_1$ (no. 33), $a = 26.0880(5)$, $b = 11.7108(2)$, $c = 18.8757(3)$ Å, $V = 5766.7(2) \text{ Å}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.40 \text{ g cm}^{-3}$, $\mu = 0.5 \text{ mm}^{-1}$, empirical absorption correction ($0.891 \leq T \leq 0.954$), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and ϕ scans, 26540 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.66 \text{ Å}^{-1}$, 13753 independent ($R_{\text{int}} = 0.053$) and 10449 observed reflections [$I \geq 2 \sigma(I)$], 701 refined parameters, $R = 0.084$, $wR^2 = 0.192$, Flack parameter $x = 0.52$ (5), max./min. residual electron density $0.84 / -0.44 \text{ e Å}^{-3}$.

Comment: Structure refined as racemic twin. Hydrogen atoms calculated and refined as riding atoms; solvent molecules refined with thermal restraints (ISOR). Hydrogen atoms at the water molecule could not be located.

Complex 7b

To a flask charged with a solution of 92 mg of **5** (0.3 mmol, 3 equiv.) in 5 mL of MeOH, a solution of 16 mg of CaAc_2 (0.1 mmol, 1 equiv.) in MeOH as well as a solution of 26 mg of $\text{TiO}(\text{acac})_2$ (0.1 mmol, 1 equiv.) and a solution of 40 mg of K_2CO_3 (0.3 mmol, 3 equiv.) were added. The mixture was stirred for 72 h. The excess of K_2CO_3 was filtered off, and the solvent was evaporated under reduced pressure. The product was obtained as a light-brown solid (82 mg, 0.08 mmol, 82 % yield). – ^1H NMR (400 MHz, CD_3OD): δ = 7.94 (s, 3H, CH=N), 7.33 (d, J = 7.7 Hz, 6H, CH_{Tol}), 7.10 (d, J = 7.7 Hz, 6H, CH_{Tol}), 6.52 (d, J = 7.5 Hz, 3H, CH_{Cat}), 6.22 (t, J = 7.5 Hz, 3H, CH_{Cat}), 5.97 (d, J = 7.5 Hz, 3H, CH_{Cat}), 2.30 (s, 9H, CH_3). – IR (neat): ν = 3377, 3191, 3053, 2321, 299, 1552, 1441, 1319, 1248, 1160, 1016, 737, 666 cm^{-1} . – MS ((–)-ESI): m/z = 999.25 [$\text{L}_3\text{TiCa-H}$] $^-$. – MS ((+)-ESI): m/z = 1038.91 [L_3TiCaK] $^+$.

Complex 7c

To a flask charged with a solution of 92 mg of **5** (0.3 mmol, 3 equiv.) in 5 mL of MeOH, a solution of 37 mg of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (0.1 mmol, 1 equiv.) in MeOH was added. Also a solution of 26 mg of $\text{TiO}(\text{acac})_2$ (0.1 mmol, 1 equiv.) and a solution of 41 mg of K_2CO_3 (0.3 mmol, 3 equiv.) were added. The mixture was stirred for 72 h. The excess of K_2CO_3 was filtered off, and the solvent was removed at 60 °C in a vacuum. The product was obtained as an orange solid (100 mg). – ^1H NMR (400 MHz, CD_3OD): δ = 7.63 (s, 3H, CH=N), 7.60 (d, J = 2.8 Hz, 6H, CH_{Tol}), 6.65 (d, J = 7.8 Hz, 6H, CH_{Tol}), 6.46 (m, 9H, CH_{Cat}), 2.14 (s, 9H, CH_3). – MS ((+)-ESI): m/z (%) = 2236.63 (85) [$\text{L}_6\text{La}_2\text{Ti}_2\text{K-2H}$] $^+$, 1123.50 (21) [$\text{L}_3\text{LaTiNaH}$] $^+$.

Acknowledgements

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