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Dicatechol-diimines: easily accessible ligands for the self-assembly of dinuclear triple-stranded helicates

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Dicatechol ligands **3b**–**g**-H_4 are simply prepared by imine formation of 2,3-dihydroxybenzaldehyde **2** with a series of different diamines **1b**–**g**. An X-ray structural analysis was obtained for the butyl-bridged compound **3e**-H_4, showing an intramolecular proton transfer and the formation of a chinoidic "keto-amine" structure. The dicatechol derivatives **3b**–**g**-H_4 form dinuclear triple-stranded helicates $M_4[(\mathbf{3})_3Ti_2]$ with titanium(IV) ions in the presence of alkali-metal carbonate. For the phenyl- and the *trans*-1,4-cyclohexyl-bridged complexes, $K_4[(\mathbf{3b})_3Ti_2]$ and $Na_4[(\mathbf{3f})_3Ti_2]$, X-ray structures were obtained.

Introduction

The self-assembly of double-[1] and triple-stranded[2] helicates is a process which has been thoroughly investigated during the last 15 years. The study of the formation, structure and properties of helicates is an easy way to gain knowledge on metal directed self-assembly processes. The basic mechanistic findings which are provided by those studies help us to understand fundamental principles of molecular recognition and self-organization which are important for the rational design of more complex superstructures. Thus, important aspects of control mechanisms for the self-assembly process as well as for the stereo- or regiochemistry of the obtained ensembles were investigated.[3]

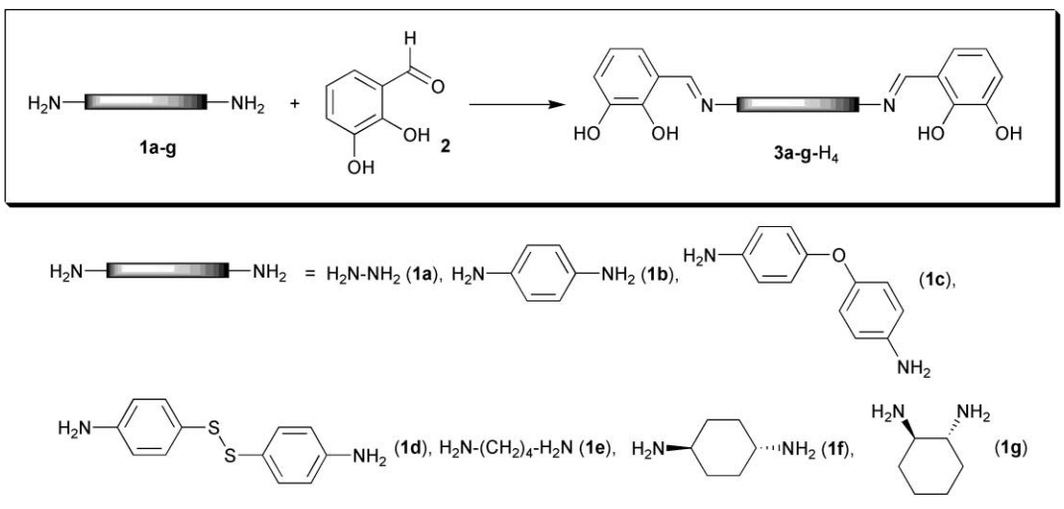
To systematically study the influences of different geometric or electronic factors on the helicate formation we need a facile way to prepare a variety of different ligands with different geometric constrains and electronic features. Hannon *et al.*,[4] Yoshida *et al.*[5] and Ziessel *et al.*[6] showed that, by simple imine condensation, bis(iminopyridine) ligands can be obtained from readily available starting materials. Such ligands form double-or triple-stranded helicates with a series of metal ions. The dinuclear complexes are not only of interest for the mechanistic and structural information we gain but also for their material properties[7] or for their ability to interact with biomolecules.[8] Related ligands with two salicylimine units were also used for coordination chemistry.[9] Just recently imine condensation was introduced by us[10] and others[11] to obtain dicatechol ligands for the formation of helicates.[12,13]

Following this work, we herein show, that imine formation is an easy entry to obtain a variety of dicatechol ligands in only one reaction step. Thus different functionalities can be easily introduced into the spacer and the ligands then can be used for the self-assembly of triple-stranded dinuclear helicates.

Results and discussion

Synthesis and characterisation of the dicatechol ligands 3a-g-H_4

Ligand **3a**-H_4 has already been reported by us.[10] The dicatechol derivatives **3b**–**g**-H_4 are prepared following two different protocols (Scheme 1). (i) The diamines **1f** or **1g**, respectively, and two equivalents of 2,3-dihydroxybenzaldehyde **2** are refluxed in toluene overnight in the presence of catalytic



Scheme 1 Preparation of dicatechol ligands **3a**–**g**-H_4 by imine condensation.

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amounts of *p*-TosOH. Water is removed by continuous distillation of the water/toluene aceotrope. After cooling to room temperature, the precipitated product is isolated by filtration and the ligands are obtained in 98% (**3f**-H_4), or 96% (**3g**-H_4) yield. (ii) The diamines **1b**, **1c**, **1d**, or **1e** and two equivalents of 2,3-dihydroxybenzaldehyde **2** are dissolved in methanol. After one day at room temperature, the precipitated diimines are isolated by filtration in 94% (**3b**-H_4), 95% (**3c**-H_4), 95% (**3d**-H_4), or 93% (**3e**-H_4)[11] yield.

The alkyl derivatives **3e**,**f**,**g**-H_4 are yellow–orange coloured, while the arylimines **3b**,**c**,**d**-H_4 are isolated as red solids. The compounds are characterized by IR, MS, elemental analysis and ^{1}H as well as ^{13}C NMR. A characteristic signal in the ^{1}H-NMR spectra (dmso-d_6) is the resonance of the imine proton, which appears in the region of δ = 8.19–9.44. In some cases we were able to observe the two OH-protons of the catechol moieties. *E.g.*, for **3e**-H_4 two signals are detected at δ = 13.77 and 8.86. The resonance at low field is assigned to the 2-hydroxy group which forms an unsymmetric intramolecular hydrogen bond to the imine with transfer of the proton to the nitrogen (*vide infra*).

Schiff bases of salicylaldehyde are well known to undergo tautomerisation and to show thermochromic and photochromic behaviour.[14] To observe this we cooled the solids in liquid nitrogen and observed a fading of the intense colour. At low temperature the hydroxy-imine form **A** is the preferred tautomer, while at higher temperature the more coloured keto-amine form **B** is favoured (Fig. 1).[14]

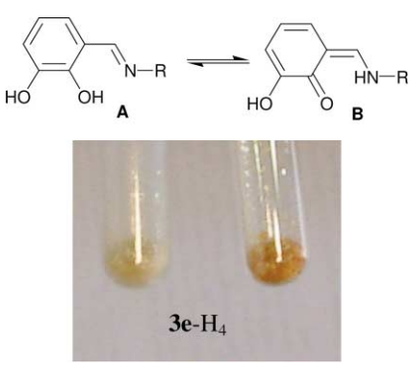


Fig. 1 Hydroxy-imine–keto-amine tautomerisation in Schiff bases of 3-hydroxysalicylaldehyde and thermochromic behaviour of **3e**-H_4: left: cooled in liquid N_2 (form **A**), right: rt (form **B**).

Crystals of **3e**-H_4 were obtained by cooling of a methanol solution of the compound. Data were collected at 223 K. The butyl bridged derivative **3e**-H_4 crystallizes in the monoclinic space group $P2_1/n$ and was refined to R = 0.047. The molecular structure of **3e**-H_4 in the solid state is presented in Fig. 2. The butyl spacer adopts a zigzag conformation and connects the two "catechol–imine" units. In the observed solid state structure those moieties adopt the tautomeric form **B**. The proton of the 2-hydroxygroup is transferred to the nitrogen and can be located by X-ray diffraction. The bond lengths which are shown in Fig. 2 support the keto-amine tautomer **B** rather then the hydroxy-imine **A**. The former C–N "imine" bond is elongated to 1.304 Å, while the C_{imine}–C_{aryl} bond is shortened to 1.413 Å. In addition, the C–O bond in 2-position of the aromatic ring with 1.292 Å is short and indicates the presence of a C=O-double bond.

The "catechol" moieties of **3e**-H_4 dimerize in an antiparallel fashion forming a 10-membered (HO–C–C–O)$_2$-ring with bifurcated hydrogen bonds. A hydrogen bonded polymer is observed in the solid state (Fig. 3). Similar dimerization behaviour was reported earlier for related Schiff bases of 3-hydroxysalicylaldehyde.[14] The obtained polymeric structure of **3e**-H_4 is structurally very similar to the hydrogen bonded polymers which are formed by crystallization of alkyl bridged di-8-hydroxyquinoline derivatives.[15]

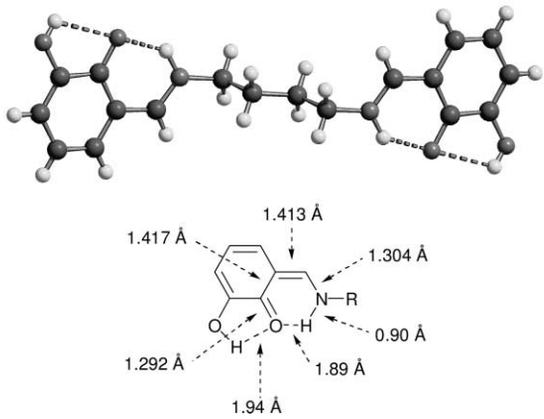


Fig. 2 Molecular structure of **3e**-H_4 in the solid state and selected bond length, which are found by X-ray structure analysis.

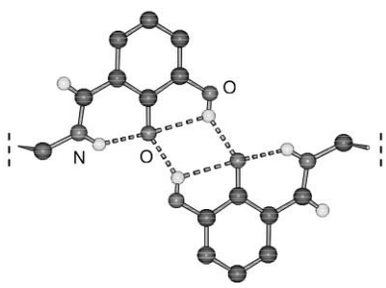
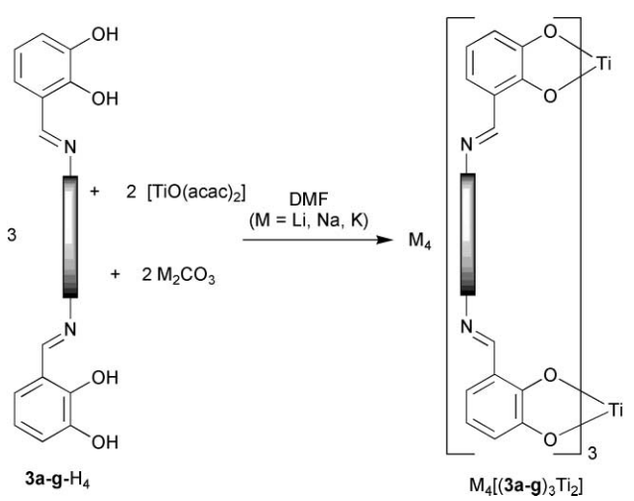


Fig. 3 The H-bonded dimerization unit in the polymeric structure of **3e**-H_4 in the solid state.

Formation of dinuclear triple stranded helicates $M_4[(3a–g)_3Ti_2]$

Titanium(IV) complexes $M_4[(\mathbf{3})_3Ti_2]$ are prepared by dissolving three equivalents of the ligand **3a**–**g**-H_4, two equivalents of $[TiO(acac)_2]$ and two equivalents of alkali metal carbonate (M = Li, Na, K) in dmf. The red solution is stirred over night at room temperature and then the solvent is removed in vacuum. Thus, the ligands **3** lead to triple-stranded dinuclear helicate-type coordination compounds (Scheme 2). The preparation and characterization of $M_4[(\mathbf{3a})_3Ti_2]$ (M = Li, Na, K) was already described by us.[10] The ligand **3e**-H_4 was used earlier for the formation of a bis-helical complex $[Cu_3(\mathbf{3e}\text{-}H_2)(\mathbf{3e})]\cdot 2H_2O$ with copper.[11]

Ligand **3b** with a phenyl spacer leads in a quantitative self-assembly process to the triple stranded dinuclear helicates $M_4[(\mathbf{3b})_3Ti_2]$ (M = Li, Na, K). In dmso-d_6 solution typical



Scheme 2 Self-assembly of triple-stranded dinuclear helicates $M_4[(\mathbf{3})_3Ti_2]$.

NMR spectra for the triple-stranded helicate $K_4[(\mathbf{3b})_3Ti_2]$ are observed {*e.g.* ^{1}H NMR: δ = 6.17 (dd, J = 7.7, 1.3 Hz, 6H), 6.36 (pseudo-t, J = 7.7 Hz, 6H), 7.00 (dd, J = 7.7, 1.3 Hz, 6H), 7.12 (s, 12H), 8.62 (s, 6H)}. Positive FAB MS (in 3-NBA) shows characteristic peaks for the dinuclear titanium complex $\{K_4[(\mathbf{3b})_3Ti_2]H^+$: m/z = 1286$\}$. The use of lithium or sodium carbonate as base leads to similar results and the dinuclear triple-stranded helicates $Li_4[(\mathbf{3b})_3Ti_2]$ and $Na_4[(\mathbf{3b})_3Ti_2]$ are obtained.

The ligands with elongated aromatic spacers **3c** and **3d** in the presence of potassium, sodium or lithium cations also lead very nicely to triple-stranded helicates $M_4[(\mathbf{3c/d})_3Ti_2]$.

On the other hand, ligands **3e**–**g** with alkyl groups in the spacer form only helicates $M_4[(\mathbf{3e}–\mathbf{g})_3Ti_2]$ if potassium or sodium are present as counter cations. The compounds are characterized by NMR, MS and elemental analysis. Due to the chirality at the spacer, ligand **3g** forms the enantiomerically pure helicates $K_4[(\mathbf{3e})_3Ti_2]$ and $Na_4[(\mathbf{3e})_3Ti_2]$.[16]

With lithium carbonate as base only broad signals can be observed by NMR spectroscopy. Those should be due to a mixture of oligomeric and polymeric coordination compounds. However, dinuclear triple-stranded complexes $Li_4[(\mathbf{3f/g})_3Ti_2]$ can be observed by ESI MS. Characteristic peaks are detected for $Li_4[(\mathbf{3f})_3Ti_2]$ at m/z = 1167 $[M - Li]^-$, 1161 $[M - 2Li + H]^-$, 1155 $[M - 3Li + 2H]^-$, 1149 $[M - 4Li + 3H]^-$, 580 $[M - 2Li]^{2-}$, 577 $[M - 3Li + H]^{2-}$, 574 $[M - 4Li + 2H]^{2-}$ and for $Li_4[(\mathbf{3g})_3Ti_2]$ at m/z = 1155 $[M - 3Li + 2H]^-$, 1149 $[M - 4Li + 3H]^-$, 577 $[M - 3Li + H]^{2-}$, 574 $[M - 4Li + 2H]^{2-}$.

As a representative example, the aromatic parts of the ^{1}H NMR spectra of $M_4[(\mathbf{3g})_3Ti_2]$ in dmso-d_6 are shown in Fig. 4. For the potassium compound $K_4[(\mathbf{3g})_3Ti_2]$ nicely resolved signals are observed at δ = 8.53 (s, imine-H), 7.02 (dd, J = 7.7, 1.5 Hz), 6.32 (t, J = 7.7 Hz), 6.10 (dd, J = 7.7, 1.5 Hz). A similar set of signals is observed for the sodium salt $Na_4[(\mathbf{3g})_3Ti_2]$ (δ = 8.59 (s), 7.02 (dd, J = 7.9, 1.5 Hz), 6.30 (t, J = 7.9 Hz), 6.06 (dd, J = 7.9, 1.5 Hz)). Only for the lithium compound can no resolved signals be detected. In the self-assembly of triple-stranded helicates from dicatechol ligands a strong templating effect seems to favour the formation of the discrete complexes in the presence of potassium or sodium cations but not in the presence of lithium. Related findings were made earlier with other dicatechol systems.[17]

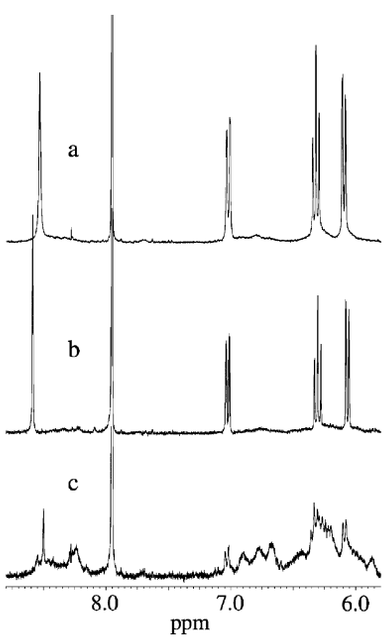


Fig. 4 Aromatic region of the ^{1}H NMR spectra of $M_4[(\mathbf{3g})_3Ti_2]$ in dmso-d_6, showing specific self-assembly in the presence of potassium (a) and sodium (b) cations and unspecific complex formation in the presence of lithium (c).

Reflections on the self-assembly of helicates from dicatechol ligands

During these coordination studies some strange observations were made. Under some conditions the self-assembly of the dinuclear triple-stranded helicates did not work. We only obtained insoluble oligomeric or polymeric material (we still did not obtain resolved NMR spectra of compounds $Li_4[(\mathbf{3e}–\mathbf{g})_3Ti_2]$). The self-assembly process seems to be highly dependent on the reaction conditions: solvent, temperature and the base seem to be strongly influencing.[18]

This raises the question, 'What are the prerequisites for the self-assembly to take place?'. One important aspect is the thermodynamically driven correction of assembly errors.[19] However, with dicatechol ligands we could show earlier that ligand exchange between coordinated and "free" ligands at room temperature takes place on a time scale of weeks.[20] The self-assembly on the other hand proceeds within hours, leading to discrete species. This seems to be a discrepancy.

We now propose that the self-assembly only works because of our special reaction conditions. The ligands and the $[TiO(acac)_2]$ are highly soluble in the solvents that are used. However, the base M_2CO_3 is not highly soluble. Therefore, first a homogeneous reaction between the ligand and the metal source takes place, liberating protons in solution. The resulting low local pH labilizes the metal complexes and leads to fast equilibria between different species. Slow heterogeneous proton capture by the base then locks the system in the thermodynamically favored state, the dinuclear triple-stranded helicate.

At the present state this interpretation is speculative and additional experiments have to be done. Furthermore, other influences, like the templating ability of different counter-cations also seem to be important.

The solid state structures of $K_4[(\mathbf{3b})_3Ti_2]$ and $Na_4[(\mathbf{3f})_3Ti_2]$

X-ray quality crystals of $K_4[(\mathbf{3b})_3Ti_2]$ and $Na_4[(\mathbf{3f})_3Ti_2]$ are obtained from (wet) dmf by slow diffusion of ether into a concentrated solution of the complexes.

The potassium salt of the titanium(IV) complex of ligand **3b**, $K_4[(\mathbf{3b})_3Ti_2]$, (Fig. 5) possesses the structure of a triple stranded dinuclear helicate, as is expected from the solution studies. Due to the rigidity of the spacer, the ligands wrap around the two titanium ions possessing only a slight helical twist (all atoms of the spacer are sp^2-hybridized).[13] The geometry at the metal centers can be described as somewhere in between a distorted octahedron and a distorted trigonal prism.[21] The long imine–

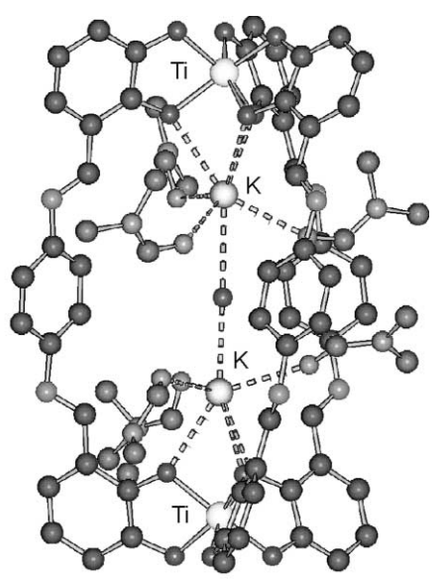


Fig. 5 Molecular structure of $\{[K_2(dmf)_6(H_2O)]\subset[(\mathbf{3b})_3Ti_2]\}^{2-}$ in the solid state (only one of the two independent molecules is shown).

aryl–imine spacers lead to a large separation of the titanium centers (Ti–Ti = 12.547/12.672 Å) and a big internal cavity results. As was observed for other catechol derived helicates, two potassium countercations are encapsulated in the interior, binding to the internal oxygen atoms of the catecholate ligands.[22,23] The imine nitrogen atoms do not interfere into cation binding but the coordination sphere at the potassium cations is saturated by binding of three dmf molecules. Additionally a water molecule is observed which bridges the two encapsulated cations.

In the solid state structure of the complex of the 1,4-*trans*-cyclohexyl-bridged ligand **3f**, a dinuclear triple-stranded helicate $Na_4[(\mathbf{3f})_3Ti_2]$ (Fig. 6) is observed as well. The cyclohexyl rings adopt a chair-type conformation and therefore possess some rigidity. Due to symmetry reasons one of the three bridging cyclohexyl rings shows positional disorder and is refined with split positions. Three of the ligands wrap around the two titanium ions and lead to a helix with a somewhat more pronounced helical twist compared to the phenyl bridged derivative. Here the Ti–Ti distance is 12.475 Å. In the solid state again two sodium cations, which each bind three dmf, are encapsulated in the helicate. Additionally two water molecules are bound to the internal sodiums, which, however, can not be resolved by X-ray crystallography. Due to the poor quality of the crystal, several atoms are split over two positions and lead to a "diffuse arrangement" of the guests in the cavity (not shown in Fig. 6).

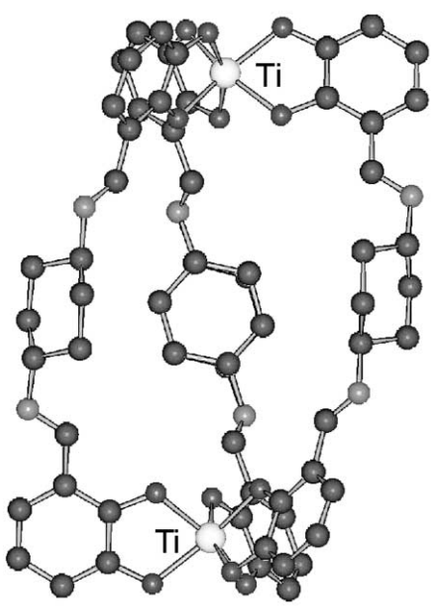


Fig. 6 Molecular structure of the tetraanion $[(\mathbf{3f})_3Ti_2]^{4-}$ in the solid state.

An important observation in the X-ray structure analyses is, that the imine moiety possesses a preferred conformation **C** (Fig. 7),[24] with the C=N double bond directed towards the "outside" of the cavity of the helicate. This is due to electrostatic attraction between the internal catecholate oxygens and the imine proton in addition to a repulsion between oxygen and imine-nitrogen lone pairs (**D**). However, an inward orientation of the imine can be observed, if coordination to an internal alkali metal cation takes place (**E**). Here the situation is very similar to the conformation of Raymond's catechol amide complexes which form an intramolecular hydrogen bond (**F**).[21]

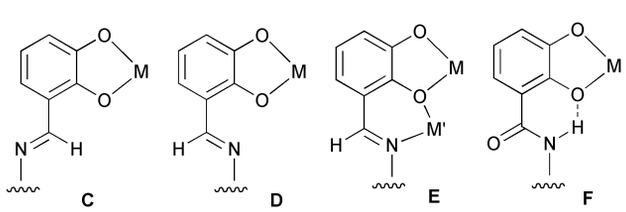


Fig. 7 Possible orientations of the imine moiety in the catecholato metal complexes **C–E** and preferred conformation of the corresponding amide **F**.

However, in solution a dynamic exchange between encapsulated and "free" countercations takes place[22] and therefore conformation **C** should be the preferred one.

Conclusion

In this paper we described a series of new, easily accessible dicatechol diimine ligands **3b–g**-H_4. The solid-state structure of **3e**-H_4 shows, that intramolecular proton transfer occurs and the compounds rather adopt the keto-amine than the hydroxy-imine form.

The ligands lead to triple-stranded dinuclear helicates with titanium(IV) ions in the presence of sodium and potassium carbonate as base. With lithium countercations only the helicates of the aryl bridged derivatives $Li_4[(\mathbf{3c–d})_3Ti_2]$ are obtained specifically. In case of alkyl spacers no defined complexes could be observed by NMR.

Two X-ray structural analyses of the triple-stranded complexes $K_4[(\mathbf{3b})_3Ti_2]$ and $Na_4[(\mathbf{3f})_3Ti_2]$ show the helicate structures.

The observations which we made during the studies invited us to speculate on the mechansim of the self-assembly process and we propose that a pH-gradient during the initial state of the self-assembly is important for the specificity of this process. Based on this proposal, we already started to investigate the process of the assembly of the helicates in detail. More experiments have to be done and we hope that we can report more exciting results in the future.

We do not believe that the presented results and discussions lead to the ultimative understanding of the self-assembly of supramolecular aggregates but it is a further part of the puzzle which we have to solve to learn how to control the build up and the shape of molecular architectures.[25]

Experimental

NMR spectra were recorded on a Bruker DRX 500, WM 400 or a Varian Inova 400 spectrometer. FT-IR spectra were recorded by diffuse reflection (KBr) on a Bruker IFS spectrometer. Mass spectra (EI, 70 eV; FAB with 3-NBA as matrix) were taken on a Finnigan MAT 90, 95 or 212 mass spectrometer. Elemental analyses were obtained with a Heraeus CHN–O-Rapid analyzer. Melting points: Büchi B-540 (uncorrected).

General procedure for the preparation of the ligands 3-H_4

Method A. 2,3-Dihydroxybenzaldehyde **2** (2 mmol) and the appropriate diamine **1** (1 mmol) are heated in toluene in the presence of catalytic amounts of *p*-TosOH. Water is removed by aceotropic distillation. After cooling to room temperature the precipitated product is isolated by filtration and is dried in vacuum.

Method B. 2,3-Dihydroxybenzaldehyde **2** (2 mmol) and the appropriate diamine **1** (1 mmol) are dissolved in 20 ml of methanol. After a few minutes an orange material precipitates, which after standing over night is isolated by filtration and dried in vacuum.

3b-H_4 (Method B): Yield: 94%; m.p. 150 °C (decomp.); ^{1}H NMR (dmso-d_6): δ = 8.96 (s, 2 H), 7.51 (s, 4 H), 7.10 (d, J = 7.8 Hz, 2 H), 6.95 (dd, J = 7.8, 1.4 Hz, 2 H), 6.78 (t, J = 7.8 Hz, 2 H); ^{13}C NMR (dmso-d_6): δ = 164.0 (CH), 149.8 (C), 146.9 (C), 146.1 (C), 123.3 (CH), 123.0 (CH), 119.9 (C), 119.5 (CH), 119.3 (CH); IR (KBr): ν = 3325, 3065, 1620, 1511, 836 cm^{-1}; MS (EI, 70 eV): m/z = 348 [M$^+$]; calcd. for

$C_{20}H_{16}N_2O_4$: C 68.96, H 4.63, N 8.04; found: C 68.77, H 4.76, N 8.25%.

3c-H$_4$ (Method B): Yield: 95%; m.p. 205 °C (decomp.); ^{1}H NMR (dmso-d$_6$): δ = 13.18 (br, 2 H), 9.19 (br, 2 H), 8.94 (s, 2 H), 7.50 (dd, J = 6.7, 2.2 Hz, 4 H), 7.15 (dd, J = 6.7, 2.2 Hz, 4 H), 7.10 (dd, J = 8.0, 1.7 Hz, 2 H), 6.95 (dd, J = 8.0, 1.7 Hz, 2 H), 6.80 (t, J = 8.0 Hz, 2 H); ^{13}C NMR (dmso-d$_6$): δ = 163.7 (CH), 156.0 (C), 149.7 (C), 146.1 (C), 144.0 (C), 123.5 (CH), 123.2 (CH), 120.0 (CH), 119.9 (C), 119.4 (CH), 119.3 (CH); IR (KBr): ν = 3463, 1619, 1499, 1463, 1371, 1279, 1249, 836, 734 cm^{-1}; MS (EI, 70 eV): m/z = 440 [M$^+$]; calcd. for $C_{26}H_{20}N_2O_5$: C 70.90, H 4.58, N 6.36; found: C 70.58, H 4.56, N 6.33%.

3d-H$_4$ (Method B): Yield: 95%; m.p. 205 °C (decomp.); ^{1}H NMR (dmso-d$_6$): δ = 12.94 (br, 2 H), 9.24 (br, 2 H), 8.93 (s, 2 H), 7.64 (d, J = 8.5 Hz, 4 H), 7.47 (d, J = 8.5 Hz, 4 H), 7.10 (d, J = 7.8 Hz, 2 H), 6.96 (d, J = 7.8 Hz, 2 H), 6.80 (t, J = 7.8 Hz, 2 H); IR (KBr): ν = 3377, 1625, 1303, 1217, 1185, 737 cm^{-1}; MS (EI, 70 eV): m/z = 488 [M$^+$]; calcd. for $C_{26}H_{20}N_2O_4S_2$: C 63.92, H 4.13, N 5.73; found: C 63.53, H 4.55, N 6.08%.

3e-H$_4$[11] (Method B): Yield: 93%; m.p. 199 °C (decomp.); ^{1}H NMR (dmso-d$_6$): δ = 8.51 (s, 2 H), 6.84 (dd, J = 7.8, 1.5 Hz, 2 H), 6.82 (dd, J = 7.8, 1.5 Hz, 2 H), 6.62 (t, J = 7.8 Hz, 2 H), 3.65 (m, 4 H), 1.73 (m, 4 H); ^{13}C NMR (dmso-d$_6$): δ = 166.6 (CH), 153.1 (C), 146.6 (C), 122.2 (CH), 118.1 (C), 117.8 (CH), 117.6 (CH), 56.9 (CH$_2$), 28.4 (CH$_2$); IR (KBr): ν = 3216, 1641, 1514, 1358, 1237, 1191, 747 cm^{-1}; MS (EI, 70 eV): m/z = 328 [M$^+$]; calcd. for $C_{18}H_{30}N_2O_4$: C 65.84, H 6.14, N 8.53; found: C 65.35, H 6.16, N 8.48%.

3f-H$_4$ (Method A): Yield: 98%; m.p. 253 °C (decomp.); ^{1}H NMR (dmso-d$_6$): δ = 8.55 (s, 2 H), 6.85 (d, J = 7.8 Hz, 2 H), 6.82 (d, J = 7.8 Hz, 2 H), 6.63 (t, J = 7.8 Hz, 2 H), 3.41 (br, 2 H), 1.92 (m, 4 H), 1.61 (m, 4 H); ^{13}C NMR (dmso-d$_6$): δ = 164.9 (CH), 152.1 (C), 146.4 (C), 122.2 (CH), 118.4 (C), 117.9 (CH, double intensity), 64.5 (CH) 32.2 (CH$_2$); IR (KBr): ν = 3212, 2942, 2854, 1636, 1544, 1518, 1464, 1361, 1235, 753 cm^{-1}; MS (EI, 70 eV): m/z = 354 [M$^+$]; calcd. for $C_{20}H_{22}N_2O_4 \cdot 1/3H_2O$: C 66.65, H 6.34, N 7.77; found: C 66.56, H 6.37, N 8.07%.

3g-H$_4$ (Method A): Yield: 96%; m.p. 85 °C; ^{1}H NMR ($CDCl_3$): δ = 8.19 (s, 2 H), 6.91 (dd, J = 7.9, 1.5 Hz, 2 H), 6.68 (dd, J = 7.9, 1.5 Hz, 2 H), 6.61 (t, J = 7.9 Hz, 2 H), 3.37 (br, 2 H), 2.02 (m, 2 H), 1.90 (m, 2 H), 1.68 (m, 2 H), 1.47 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ = 165.0 (CH), 152.9 (C), 145.7 (C), 122.4 (CH), 117.7 (CH), 116.8 (CH), 116.7 (C), 70.6 (CH) 32.8 (CH$_2$), 24.0 (CH$_2$); IR (KBr): ν = 3351, 2936, 2860, 1631, 1465, 1271, 1228, 735 cm^{-1}; MS (EI, 70 eV): m/z = 354 [M$^+$]; calcd. for $C_{20}H_{22}N_2O_4$: C 67.78, H 6.26, N 7.90; found: C 67.62, H 6.42, N 7.54%.

General procedure for the preparation of the complexes M$_4$[(3)$_3$Ti$_2$]

Three equivalents of ligand **3**-H$_4$, two equivalents of TiO(acac)$_2$ and two equivalents of M_2CO_3 (M = Li, Na, K) are dissolved in dmf and the red solution is stirred over night. Solvent is removed to obtain the dinuclear complexes M$_4$[(**3**)$_3$Ti$_2$].

K$_4$[(3b)$_3$Ti$_2$]. Prepared in methanol as solvent. Quant.; ^{1}H NMR (dmso-d$_6$): δ = 8.62 (s, 6 H), 7.12 (s, 12 H), 7.00 (dd, J = 8.0, 1.1 Hz, 6 H), 6.36 (t, J = 8.0 Hz, 6 H), 6.17 (dd, J = 8.0, 1.1 Hz, 6 H); ^{13}C NMR (dmso-d$_6$): δ = 164.4 (C), 161.2 (C), 158.2 (CH), 151.3 (C), 122.5 (CH), 118.8 (C), 116.7 (CH), 113.8 (CH), 112.2 (CH); IR (KBr): ν = 3365, 3050, 1612, 1550, 1494 cm^{-1}; MS (pos. FAB, 3-NBA): m/z = 1286 [MH$^+$]; calcd. for $C_{60}H_{36}K_4N_6O_{12}Ti_2 \cdot 3H_2O \cdot 4MeOH$: C 52.39, H 3.98, N 5.73; found: C 52.85, H 3.75, N 5.82%.

K$_4$[(3c)$_3$Ti$_2$]. Quant.; ^{1}H NMR (dmso-d$_6$): δ = 8.66 (s, 6 H), 7.19 (d, J = 8.7 Hz, 12 H), 7.04 (d, J = 8.2 Hz, 6 H), 6.95 (d, J = 8.7 Hz, 12 H), 6.38 (t, J = 8.2 Hz, 6 H), 6.16 (d, J = 8.2 Hz, 6 H); IR (KBr): ν = 3426, 1662, 1612, 1494, 1443, 1386, 1249, 847, 741 cm^{-1}; calcd. for $C_{78}H_{48}K_4N_6O_{15}Ti_2 \cdot 3H_2O \cdot 4dmf$: C 56.66, H 4.33, N 7.34; found: C 56.78, H 4.47, N 7.04%.

Na$_4$[(3c)$_3$Ti$_2$]. Quant.; ^{1}H NMR (dmso-d$_6$): δ = 8.66 (s, 6 H), 7.14 (d, J = 8.6 Hz, 12 H), 7.04 (dd, J = 7.9, 1.5 Hz, 6 H), 6.94 (d, J = 8.6 Hz, 12 H), 6.37 (t, J = 7.9 Hz, 6 H), 6.15 (dd, J = 7.9, 1.5 Hz, 6 H); IR (KBr): ν = 3432, 1662, 1494, 1445, 1385, 1249, 847, 743 cm^{-1}; calcd. for $C_{78}H_{48}Na_4N_6O_{15}Ti_2 \cdot 5H_2O \cdot 5dmf$: C 57.21, H 4.80, N 7.89; found: C 57.55, H 4.81, N 7.80%.

Li$_4$[(3c)$_3$Ti$_2$]. Quant.; ^{1}H NMR (dmso-d$_6$): δ = 8.62 (s, 6 H), 7.13 (d, J = 8.9 Hz, 12 H), 7.00 (dd, J = 8.0, 1.5 Hz, 6 H), 6.95 (d, J = 8.9 Hz, 12 H), 6.34 (t, J = 7.9 Hz, 6 H), 6.12 (dd, J = 8.0, 1.5 Hz, 6 H); IR (KBr): ν = 3426, 1664, 1613, 1494, 1444, 1384, 1250, 1186, 844, 742 cm^{-1}; calcd. for $C_{78}H_{48}Li_4N_6O_{15}Ti_2 \cdot 5H_2O \cdot 6dmf$: C 58.78, H 5.14, N 8.57; found: C 59.05, H 5.15, N 8.65%.

K$_4$[(3d)$_3$Ti$_2$]. Quant.; ^{1}H NMR (dmso-d$_6$): δ = 8.62 (s, 6 H), 7.50 (d, J = 8.0 Hz, 12 H), 7.18 (d, J = 8.0 Hz, 12 H), 7.04 (d, J = 7.7 Hz, 6 H), 6.37 (t, J = 7.7 Hz, 6 H), 6.17 (d, J = 7.7 Hz, 6 H); IR (KBr): ν = 3447, 1661, 1490, 1443, 1407, 1251, 1204, 740, 613, 514 cm^{-1}; calcd. for $C_{78}H_{48}K_4N_6O_{12}S_6Ti_2 \cdot 3H_2O \cdot 4dmf$: C 52.67, H 4.03, N 6.82; found: C 52.43, H 4.58, N 6.68%.

Na$_4$[(3d)$_3$Ti$_2$]. Quant.; ^{1}H NMR (dmso-d$_6$): δ = 8.61 (s, 6 H), 7.49 (d, J = 8.7 Hz, 12 H), 7.15 (d, J = 8.7 Hz, 12 H), 7.02 (dd, J = 7.9, 1.5 Hz, 6 H), 6.36 (t, J = 7.9 Hz, 6 H), 6.19 (d, J = 7.9, 1.5 Hz, 6 H); IR (KBr): ν = 3428, 1662, 1611, 1489, 1444, 1385, 1251, 1206, 740, 615, 519 cm^{-1}; calcd. for $C_{78}H_{48}Na_4N_6O_{12}S_6Ti_2 \cdot 4H_2O \cdot 4dmf$: C 53.89, H 4.22, N 6.98; found: C 53.88, H 4.56, N 7.22%.

Li$_4$[(3d)$_3$Ti$_2$]. Quant.; ^{1}H NMR (dmso-d$_6$): δ = 8.63 (s, 6 H), 7.45 (d, J = 8.5 Hz, 12 H), 7.16 (d, J = 8.5 Hz, 12 H), 7.07 (d, J = 8.0 Hz, 6 H), 6.34 (t, J = 8.0 Hz, 6 H), 6.22 (d, J = 8.0 Hz, 6 H); IR (KBr): ν = 3436, 1662, 1591, 1549, 1490, 1444, 1385, 1252, 1207, 1187, 742, 620, 520, cm^{-1}; calcd. for $C_{78}H_{48}Li_4N_6O_{12}S_6Ti_2 \cdot 6H_2O \cdot 4dmf$: C 54.66, H 4.49, N 7.08; found: C 54.79, H 4.42, N 7.00%.

K$_4$[(3e)$_3$Ti$_2$]. Quant.; ^{1}H NMR (dmso-d$_6$): δ = 8.49 (s, 6 H), 6.88 (dd, J = 7.7, 1.5 Hz, 6 H), 6.30 (t, J = 7.7 Hz, 6 H), 6.08 (dd, J = 7.7, 1.5 Hz, 6 H), 3.53 (m., 12 H), 1.63 (m, 12 H); IR (KBr): ν = 3434, 1659, 1590, 1444, 1386, 1250, 1214, 740, 663, 517 cm^{-1}; MS (neg. FAB, 3-NBA): m/z = 1185 [M − K]$^-$, 573 [M − 2K]$^{2-}$, 369 [M − 3K]$^{3-}$; calcd. for $C_{54}H_{48}K_4N_6O_{12}Ti_2 \cdot 2H_2O \cdot 2dmf$: C 51.20, H 4.73, N 7.89; found: C 51.12, H 5.25, N 7.86%.

Na$_4$[(3e)$_3$Ti$_2$]. Quant.; ^{1}H NMR (dmso-d$_6$): δ = 8.52 (s, 6 H), 6.89 (dd, J = 7.9, 1.5 Hz, 6 H), 6.31 (t, J = 7.9 Hz, 6 H), 6.09 (dd, J = 7.9, 1.5 Hz, 6 H), 3.52 (m., 12 H), 1.64 (m, 12 H); IR (KBr): ν = 1667, 1636, 1591, 1446, 1387, 1253, 1213, 761, 738, 661 cm^{-1}; MS (neg. FAB, 3-NBA): m/z = 1137 [M − Na]$^-$, 557 [M − 2Na]$^{2-}$, 364 [M − 3Na]$^{3-}$; calcd. for $C_{54}H_{48}Na_4N_6O_{12}Ti_2 \cdot 3H_2O \cdot 3dmf$: C 52.76, H 5.27, N 8.79; found: C 52.52, H 5.30, N 8.23%.

K$_4$[(3f)$_3$Ti$_2$]. Quant.; ^{1}H NMR (dmso-d$_6$): δ = 8.58 (s, 6 H), 6.87 (dd, J = 7.7, 1.7 Hz, 6 H), 6.29 (t, J = 7.7 Hz, 6 H), 6.08 (dd, J = 7.7, 1.7 Hz, 6 H), 1.93 (m, 12 H), 1.58 (m, 12 H), the signal of the alkyl-methyne proton is probably hidden under a water peak; IR (KBr): ν = 2948, 1647, 1596, 1550, 1481, 1249, 1217, 747 cm^{-1}; MS (neg. ESI-MS, methanol): m/z = 1263 [M − K]$^-$, 1187 [M − 3K + 2H]$^-$, 1149 [M − 4K + 3H]$^-$, 612 [M − 2K]$^{2-}$; calcd. for $C_{60}H_{54}K_4N_6O_{12}Ti_2 \cdot 10H_2O$: C 48.58, H 5.03, N 5.67; found: C 48.55, H 4.93, N 4.59%.

Na$_4$[(3f)$_3$Ti$_2$]. Quant.; ^{1}H NMR (dmso-d$_6$): δ = 8.61 (s, 6 H), 6.85 (dd, J = 7.7, 1.5 Hz, 6 H), 6.28 (t, J = 7.7 Hz, 6 H), 6.07 (dd, J = 7.7, 1.5 Hz, 6 H), 3.40 (br, 6 H), 1.86 (m, 12 H), 1.55 (m, 12

Table 1 Crystallographic summary for compounds **3e**-H_4, $K_4[(\mathbf{3b})_3Ti_2]$ and $Na_4[(\mathbf{3f})_3Ti_2]$

	3e-H_4	$K_4[(\mathbf{3b})_3Ti_2]$	$Na_4[(\mathbf{3f})_3Ti_2]$
Chemical formula	$C_{18}H_{20}N_2O_4$	$[K_4(C_{60}H_{36}N_6O_{12}Ti_2)]_2 \cdot 19C_3H_7NO \cdot 5H_2O$	$Na_4(C_{60}H_{54}N_6O_{12}Ti_2) \cdot 10C_3H_7NO \cdot 2H_2O$
Formula weight	328.36	4049.20	2005.84
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$C2/c$
a/Å	7.203(1)	18.631(1)	18.381(1)
b/Å	8.565(1)	24.296(1)	22.989(1)
c/Å	13.656(1)	25.448(1)	25.438(1)
α/°	90.00	113.82(1)	90.00
β/°	102.72(1)	102.61(1)	110.98(1)
γ/°	90.00	91.95(1)	90.00
V/Å^3	821.8(2)	10187.0(8)	10036.5(8)
Z	2	2	4
T/K	223	198	198
μ/cm^{-1}	7.77	3.96	2.55
No. data collected	2256	74509	19109
No. unique data	1317	26550	6521
$R_{int.}$	0.053	0.090	0.057
Final $R(\|F\|)$ for $F_o > 2\sigma(F_o)$	0.047	0.092	0.148
Final $R(F^2)$ for all data	0.118	0.270	0.318

H); IR (KBr): ν = 3413, 2929, 2858, 1635, 1539, 1550, 1493, 1446, 1251, 1215, 743 cm^{-1}; MS (neg. ESI-MS, methanol): m/z = 1215 $[M - Na]^-$, 1193 $[M - 2Na + H]^-$, 1171 $[M - 3Na + 2H]^-$, 596 $[M - 2Na]^{2-}$, 585 $[M - 3Na + H]^{2-}$, 574 $[M - 4Na + 2H]^{2-}$; calcd. for $C_{60}H_{54}Na_4N_6O_{12}Ti_2 \cdot 10H_2O$: C 50.79, H 5.26, N 5.92; found: C 50.48, H 5.04, N 4.78%.

$Li_4[(\mathbf{3f})_3Ti_2]$. 86% yield; ^{1}H NMR (dmso-d_6): No resolved NMR spectrum can be obtained for $Li_4[(\mathbf{3f})_3Ti_2]$; IR (KBr): ν = 3366, 2932, 2860, 1643, 1595, 1549, 1494, 1447, 1251, 1216, 743 cm^{-1}; MS (neg. ESI-MS, methanol): m/z = 1167 $[M - Li]^-$, 1161 $[M - 2Li + H]^-$, 1155 $[M - 3Li + 2H]^-$, 1149 $[M - 4Li + 3H]^-$, 580 $[M - 2Li]^{2-}$, 577 $[M - 3Li + H]^{2-}$, 574 $[M - 4Li + 2H]^{2-}$; calcd. for $C_{60}H_{54}Li_4N_6O_{12}Ti_2 \cdot 10H_2O$: C 53.19, H 5.51, N 6.20; found: C 53.10, H 5.24, N 5.55%.

$K_4[(\mathbf{3g})_3Ti_2]$. Quant.; ^{1}H NMR (dmso-d_6): δ = 8.53 (s, 6 H), 7.02 (dd, J = 7.7, 1.5 Hz, 6 H), 6.32 (t, J = 7.7 Hz, 6 H), 6.10 (dd, J = 7.7, 1.5 Hz, 6 H), 3.19 (m, 6 H), 2.09 (m, 12 H), 1.49 (m, 6 H), 1.28 (m, 6 H); IR (KBr): ν = 3402, 3056, 2930, 2858, 1656, 1446, 1251, 1217, 742, 676 cm^{-1}; MS (neg. ESI-MS, methanol): m/z = 1263 $[M - K]^-$, 1225 $[M - 2K + H]^-$, 1187 $[M - 3K + 2H]^-$, 1149 $[M - 4K + 3H]^-$, 612 $[M - 2K]^{2-}$, 593 $[M - 3K + H]^{2-}$, 574 $[M - 4K + 2H]^{2-}$; calcd. for $C_{60}H_{54}K_4N_6O_{12}Ti_2 \cdot 6H_2O$: C 51.06, H 4.71, N 5.95; found: C 51.30, H 5.24, N 5.25%.

$Na_4[(\mathbf{3g})_3Ti_2]$. Quant.; ^{1}H NMR (dmso-d_6): δ = 8.59 (s, 6 H), 7.02 (dd, J = 7.9, 1.5 Hz, 6 H), 6.30 (t, J = 7.9 Hz, 6 H), 6.06 (dd, J = 7.9, 1.5 Hz, 6 H), 3.25 (m, 6 H), 2.14 (m, 12 H), 1.49 (m, 6 H), 1.26 (m, 6 H); IR (KBr): ν = 3366, 3056, 2929, 2858, 1662, 1591, 1447, 1252, 1215, 741, 668 cm^{-1}; MS (neg. ESI-MS, methanol): m/z = 1215 $[M - Na]^-$, 1193 $[M - 2Na + H]^-$, 1171 $[M - 3Na + 2H]^-$, 1149 $[M - 4Na + 3H]^-$, 585 $[M - 3Na + H]^{2-}$, 574 $[M - 4Na + 2H]^{2-}$; calcd. for $C_{60}H_{54}Na_4N_6O_{12}Ti_2 \cdot 9H_2O$: C 51.44, H 5.18, N 6.00; found: C 51.71, H 5.39, N 4.91%.

$Li_4[(\mathbf{3g})_3Ti_2]$. Quant.; ^{1}H NMR (dmso-d_6): no resolved NMR spectrum could be obtained for $Li_4[(\mathbf{3g})_3Ti_2]$; IR (KBr): ν = 3393, 3056, 1935, 2860, 1645, 1595, 1493, 1448, 1252, 1217, 745 cm^{-1}; MS (neg. ESI-MS, methanol): m/z = 1155 $[M - 3Li + 2H]^-$, 1149 $[M - 4Li + 3H]^-$, 577 $[M - 3Li + H]^{2-}$, 574 $[M - 4Li + 2H]^{2-}$; calcd. for $C_{60}H_{54}Li_4N_6O_{12}Ti_2 \cdot 8H_2O$: C 54.64, H 5.35, N 6.37; found: C 54.87, H 5.76, N 5.76%.

Crystallography

A summary of the crystal data, data collection and refinement parameters for compounds **3e**-H_4, $K_4[(\mathbf{3b})_3Ti_2]$ and $Na_4[(\mathbf{3f})_3Ti_2]$ are given in Table 1.

Data sets were collected on Nonius Kappa CCD diffractometers, one equipped with a rotating anode generator Nonius FR591 (Mo-radiation). Programs used: data collection - COLLECT,[26] data reduction - Denzo-SMN,[27] absorption correction - SORTAV,[28] structure solution - SHELXS-97,[29] structure refinement - SHELXL-97,[30] graphics - SCHAKAL[31] and XP.[32]

CCDC reference numbers 212460, 212461 and 220089.

See http://www.rsc.org/suppdata/dt/b3/b311483j/ for crystallographic data in CIF or other electronic format.

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References

1 J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier and D. Moras, *Proc. Natl. Acad. Sci. USA*, 1987, **84**, 2565; J.-M. Lehn and A. Rigault, *Angew. Chem.*, 1988, **100**, 1121; J.-M. Lehn and A. Rigault, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1095.

2 A. F. Williams, C. Piguet and G. Bernardinelli, *Angew. Chem.*, 1991, **103**, 1530; A. F. Williams, C. Piguet and G. Bernardinelli, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1490; R. Krämer, J.-M. Lehn, A. DeCian and J. Fischer, *Angew. Chem.*, 1993, **105**, 764; R. Krämer, J.-M. Lehn, A. DeCian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 703.

3 E. C. Constable, *Tetrahedron*, 1992, **48**, 10013; C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; M. Albrecht, *Chem. Eur. J.*, 2000, **6**, 3485; M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457.

4 M. J. Hannon, C. L. Painting, A. Jackson, J. Hamblin and W. Errington, *Chem. Commun.*, 1997, 1807; M. J. Hannon, C. L. Painting and W. Errington, *Chem. Commun.*, 1997, 307; M. J. Hannon, C. L. Painting and N. W. Alcock, *Chem. Commun.*, 1999, 2023; J. Hamblin, L. J. Childs, N. W. Alcock and M. J. Hannon, *J. Chem. Soc., Dalton Trans.*, 2002, 164; F. Tuna, J. Hamblin, A. Jackson, G. Clarkson, N. W. Alcock and M. J. Hannon, *Dalton Trans.*, 2003, 2141.

5 N. Yoshida, H. Oshio and T. Ito, *Chem. Commun.*, 1998, 63; N. Yoshida and K. Ichikawa, *Chem. Commun.*, 1997, 1091.

6 R. Ziessel, A. Harriman, J. Suffert, M. T. Youinou, A. De Cian and J. Fischer, *Angew. Chem.*, 1997, **109**, 2612; R. Ziessel, A. Harriman, J. Suffert, M. T. Youinou, A. De Cian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2509; A. El-ghayouy, L. Douce, A. Skoulios and R. Ziessel, *Angew. Chem.*, 1998, **110**, 2327; A. El-ghayouy, L. Douce, A. Skoulios and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 2205; R. Ziessel, A. Harriman, A. El-ghayouy, L. Douce, E. Leize, H. Nierengarten and A. Van Dorsselaer, *New J. Chem.*, 2000, **24**, 729.

7 R. Ziessel, *Coord. Chem. Rev.*, 2001, **216/217**, 195.
8 I. Meistermann, V. Moreno, M. J. Prieto, E. Moldrheim, E. Sletten, S. Khalid, P. M. Rodger, J. C. Peberdy, C. J. Isaac, A. Rodger and M. J. Hannon, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 5069; M. J. Hannon, V. Moreno, M. J. Prieto, E. Moldrheim, E. Sletten, I. Meistermann, C. J. Isaac, K. J. Sanders and A. Rodger, *Angew. Chem.*, 2001, **113**, 904; M. J. Hannon, V. Moreno, M. J. Prieto, E. Moldrheim, E. Sletten, I. Meistermann, C. J. Isaac, K. J. Sanders and A. Rodger, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 879.
9 N. Yoshida, H. Oshio and T. Ito, *J. Chem. Soc., Perkin Trans. 2*, 1999, 975; S. Mizukami, H. Houjou, Y. Nagawa and M. Kanesato, *Chem. Commun.*, 2003, 1148.
10 M. Albrecht, S. Kamptmann and R. Fröhlich, *Polyhedron*, 2003, **22**, 643.
11 J. Sanmartin, M. R. Bermejo, A. M. Garcia-Deibe, O. Piro and E. E. Castellano, *Chem. Commun.*, 1999, 1953.
12 E. J. Enemark and T. D. P. Stack, *Angew. Chem.*, 1995, **107**, 1082; E. J. Enemark and T. D. P. Stack, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 996; E. J. Enemark and T. D. P. Stack, *Angew. Chem.*, 1998, **110**, 977; E. J. Enemark and T. D. P. Stack, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 932; E. J. Enemark and T. D. P. Stack, *Inorg. Chem.*, 1996, **35**, 2719; M. Albrecht, *Chem. Soc. Rev.*, 1998, **27**, 281.
13 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.
14 H. Pizzala, M. Carles, W. E. E. Stone and A. Thevand, *J. Chem. Soc., Perkin Trans. 2*, 2000, 935.
15 M. Albrecht, O. Blau, E. Wegelius and K. Rissanen, *New J. Chem.*, 1999, 667; M. Albrecht, O. Blau, K. Witt, E. Wegelius, M. Nissinen and K. Rissanen, *Synthesis*, 1999, 1819.
16 V. Amendola, L. Fabbrizzi, P. Pallavicini, E. Sartirana and A. Taglietti, *Inorg. Chem.*, 2003, **42**, 1632; V. Amendola, L. Fabbrizzi, E. Mundum and P. Pallavicini, *Dalton Trans.*, 2003, 773; P. Pallavicini, V. Amendola, Y. D. Fernandez, M. Ghisalberti, L. Linati, C. Mangano, A. M. Lanfredi and C. Massera, *Dalton Trans.*, 2003, 575.
17 M. Albrecht and S. Kotila, *Chem. Commun.*, 1996, 2309; M. Albrecht and O. Blau, *Chem. Commun.*, 1997, 345; M. Albrecht, O. Blau and R. Fröhlich, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 4876.
18 M. Albrecht, M. Schneider and H. Röttele, *Chem. Ber.*, 1997, **130**, 615.
19 J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; D. Philp and J. F. Stoddart, *Angew. Chem.*, 1996, **108**, 1242; D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1154.
20 M. Albrecht, *Chem. Eur. J.*, 1997, **3**, 1466.
21 T. B. Karpishin, T. D. P. Stack and K. N. Raymond, *J. Am. Chem. Soc.*, 1993, **115**, 182.
22 M. Albrecht, H. Röttele and P. Burger, *Chem. Eur. J.*, 1996, **2**, 1264.
23 M. Albrecht, M. Schneider and R. Fröhlich, *New J. Chem.*, 1998, 753.
24 M. Albrecht, I. Janser, H. Houjou, R. Fröhlich, submitted for publication.
25 S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; D. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975.
26 COLLECT, Nonius B.V., Delft, The Netherlands, 1998.
27 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307.
28 R. H. Blessing, *Acta Crystallogr.*, 1995, **A51**, 33; R. H. Blessing, *J. Appl. Crystallogr.*, 1997, **30**, 421.
29 G. M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467; G. M. Sheldrick, SHELXS-97, Program for solution of crystal structures, University of Göttingen, Germany, 1997.
30 G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.
31 E. Keller, SCHAKAL, University of Freiburg, Germany, 1997.
32 XP, Bruker AXS, Madison, WI, 2001.