Long-Range Stereocontrol in the Self-Assembly of Two-Nanometer-Dimensioned Triple-Stranded Dinuclear Helicates[+]

Markus Albrecht,*[a] Ingo Janser,[a] Hirohiko Houjou,[b] and Roland Fröhlich[c]

Dedicated to Professor János Rétey on the occasion of his 70th birthday

Abstract: A series of bisimine-bridged dicatechol ligands **2-H$_4$**–**5-H$_4$** were synthesized and were used to prepare triple-stranded dinuclear helicate-type complexes with a length of up to more than 2 nm. X-ray structural analyses of $Na_4[(\mathbf{2})_3V_2]$, $Na_4[(\mathbf{3})_3Ti_2]$, $Na_4[(\mathbf{4})_3Ti_2]$, and $Na_4[(\mathbf{5})_3Ti_2]$, as well as temperature-dependent NMR investigations of $Na_4[(\mathbf{4})_3Ti_2]$ and $Na_4[(\mathbf{5})_3Ti_2]$ show that, in the case of the rigid linear ligands **2** and **3**, and of the ligand **5**, which possesses C_{2h} symmetry in its idealized structure, homochiral helicates are diastereoselectively formed. Ligand **4**, on the other hand, with idealized C_{2v} symmetry, leads with surprisingly high selectivity to the formation of the heterochiral *meso*-helicate. This is attributed to the ability of ligand **4** to adopt a less-restricted conformation in the *meso* compound than in the helical complex. NMR investigations indicate that both complex units of $Na_4[(\mathbf{4})_3Ti_2]$ invert ($\Lambda\Delta \rightarrow \Delta\Lambda$) simultaneously, while in the case of $Na_4[(\mathbf{5})_3Ti_2]$ a stepwise racemization proceeds.

Keywords: helicates · self-assembly · stereoselectivity · titanium · vanadium

Introduction

(Metallo-)supramolecular chemistry[1] is a discipline which is positioned at the borders between chemistry and nanotechnology.[2] It provides the chemical tools for, and the mechanistic understanding of, arranging molecular components to give large, very stable noncovalently linked structures.[3] The knowledge of fundamental mechanistic principles of coordination chemistry,[4] supramolecular chemistry,[5] and self-assembly[6] are essential for the systematic use of the chemical "bottom up synthesis"[7] for metal-containing nanostructures.

Modern coordination chemistry started with the groundbreaking work of Alfred Werner in the late 19th century. Basic knowledge of the three-dimensional arrangement of ligands coordinated to metal ions was provided at this time.[8] An extension of this "simple" coordination chemistry towards more complex and larger self-assembled structures was introduced in the 1980s by Lehn and co-workers.[9,10] This was, and still is, thoroughly investigated by the groups of Raymond,[11–13] Saalfrank,[12,14,15] Constable,[16,17] Ward,[18] and many others.[7,19] An even more sophisticated level of organization is achieved in the preparation of large, multinanometer-dimensioned oligo- (or better: poly-) nuclear coordination compounds which approach the size of proteins or viruses.[20] This is impressively demonstrated by the work of Stang,[21] Fujita,[22] Robson[23] and their respective coworkers.

As it is understood today, the specificity of the self-assembly of metallo-supramolecular architectures depends on the symmetry of the molecular components; on the one hand on the coordination geometry of the metals, and on the other on the symmetry of the ligands.[5] However, for the in-depth study of the basic mechanistic principles of the self-assembly of supramolecular aggregates by metal coordination, simple model compounds have to be studied. This allows the use of the gained knowledge to design bigger supermolecules. Therefore, during the last 15 years, helicates became a kind of "metallo-supramolecular chemists' drosophila", which made it easy to investigate self-assembly processes using coordination chemistry.[10,24,25]

The mechanism of the self-assembly of helicates,[25–28] the "cooperativity" of this process,[29] and "secondary interac-

[a] Prof. Dr. M. Albrecht, I. Janser
Institut für Organische Chemie der RWTH
Prof.-Pirlet-Strasse 1, 52074 Aachen (Germany)
Fax: (+49) 241-80-92385
E-mail: markus.albrecht@oc.rwth-aachen.de

[b] Dr. H. Houjou
National Institute of Advanced Industrial Science and Technology (AIST)
Tsukuba Central 4. 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562 (Japan)

[c] Dr. R. Fröhlich
Organisch Chemisches Institut der Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)

[+] This work was supported by the Fonds der Chemischen Industrie. We thank Dr. J. Runsink for the temperature-dependent NMR measurements. Support by the SFB 380 is gratefully acknowledged.

 DOI: 10.1002/chem.200305602

tions" (templating effects)[10,30,31] have already been the focus of much work. Further questions regarding the orientation of directional ligands[17,32–34] or the self- or hetero-recognition of ligands and/or metals[35] were also posed. Just recently several groups have started to investigate the function of helicates with respect to electrochemistry,[36] photophysics,[34,37,38] mesoscopic behavior,[39] and their ability to recognize guests[40] or binding sites.[41]

In the self-assembly of double- and triple-stranded helicates, an intrinsically chiral supramolecular architecture is formed from achiral components (if ligands without stereogenic units are used).[10] Chirality is introduced upon wrapping of the helicating ligands around the metal centers. In the case of the *meso*-helicates[31,42–46] ("side-by-side complexes",[47] or"mesocates"[48]) an achiral supermolecule is obtained that bears two oppositely configured chiral units. Different factors can be responsible for the stereocontrol in the formation of the helicate-type complexes.[49] Templating effects might influence the diastereoselective formation of helicates.[15,48,50] Chiral units in the ligand spacer can control the stereochemistry at the metal complex units,[51] or steric constraints enforce one of the two possible diastereomeric forms of coordination compounds.[28,52]

As a systematic entry for the stereospecific preparation of helicates or *meso*-helicates, we introduced the "even–odd principle"[53] in this field of chemistry: We prepared alkyl-bridged dicatechol,[54] di-8-hydroxyquinoline,[55] or dibipyridine[43] ligands with alkyl spacers of different length (e.g. **1a-H$_4$**, **1b-H$_4$**), and owing to the preferred zigzag conformation of the alkyl chain, the diastereoselectivity of the complex formation can be controlled.[45]

As outlined for the "CH_2" spacer of **1a-H$_4$** in Figure 1, ligands with an odd number of methylene units in the spacer possess a "horizontal" mirror plane as the most influential symmetry element of the idealized C_{2v} symmetry, which mirors the two attached chiral metal-complex moieties onto each other. This symmetry transformation leads to an opposite configuration at the complex units, and thus the ligand is predisposed to form the achiral dinuclear *meso*-helicate $\Lambda\Delta$-[(**1a**)$_3$Ti$_2$]$^{4-}$.[31] The methylene unit also possesses a C_2-symmetry axis. However, to preserve this symmetry in a dinuclear complex with short spacers, the ligand has to adopt an unfavorable conformation for complex formation. If long spacers are present, this conformation should not be "unfavorable" (vide infra).

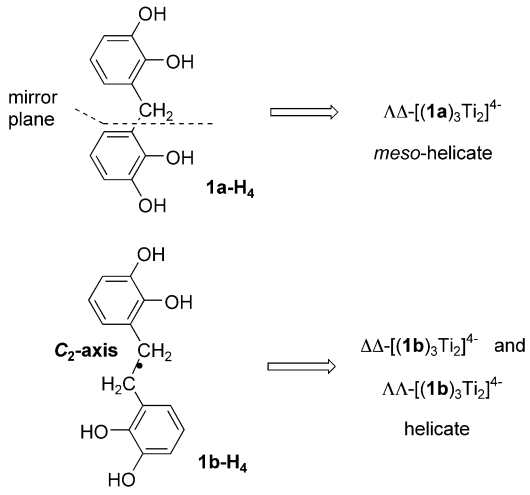


Figure 1. Idealized representation of the ligands **1a-H$_4$** and **1b-H$_4$** showing the symmetry elements that are relevant for the selective formation of the *meso*-helicate (mesocate, side-by-side complex) [(**1a**)$_3$Ti$_2$]$^{4-}$[31] or the helicate [(**1b**)$_3$Ti$_2$]$^{4-}$.[56]

Ligands with an even number of methylene units, such as **1b-H$_4$**, show idealized C_{2h} symmetry. They possess a C_2 axis (see Figure 1) as the relevant symmetry element. This leads to the specific formation of chiral helicates such as $\Lambda\Lambda$- and $\Delta\Delta$-[(**1b**)$_3$Ti$_2$]$^{4-}$ as a racemic mixture.[56] Thus, the alkyl chains of ligands with a linear alkyl bridge connecting two rigid metal binding sites act as stereo-controlling units that transfer the chiral information from one metal-complex moiety to the other and predetermine the stereochemical relation (homo- versus heterochiral) between the two centers.[57]

In the present study we synthesized a series of dicatechol ligands **2**–**5** (see Scheme 1) by simple imine condensation[33,58–63] and prepared their dinuclear metal complexes.[64] Our aim was to assemble nanometer-dimensioned complexes, and to use the most simple "stereo-controlling" alkyl units—methylene and ethylene—in conjunction with rigid linear connectors to control the formation of stereochemically well-defined coordination compounds.[65] We wanted to determine whether the relative stereochemistry is still controlled by the methylene or ethylene units (Figure 2), as was described for ligands **1a** and **1b**.[31,45,56]

The small control units CH_2 and $(CH_2)_2$ are therefore introduced in the central part of a long, partly rigid spacer to

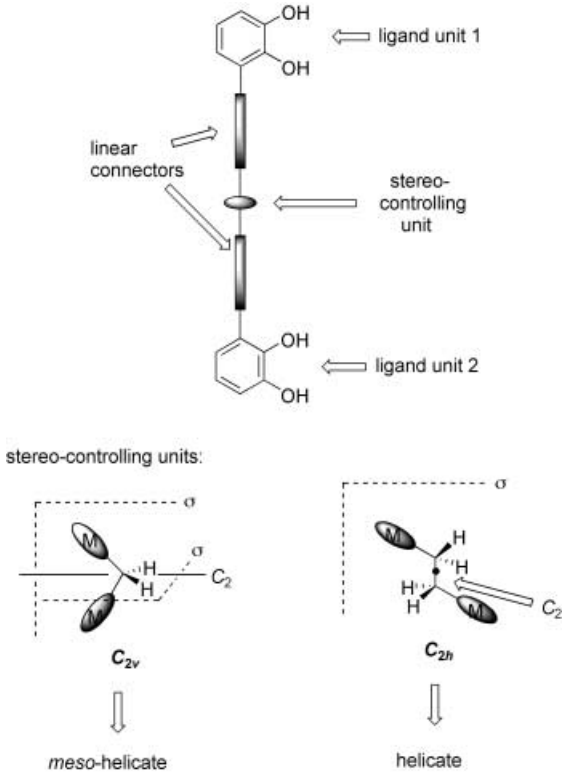
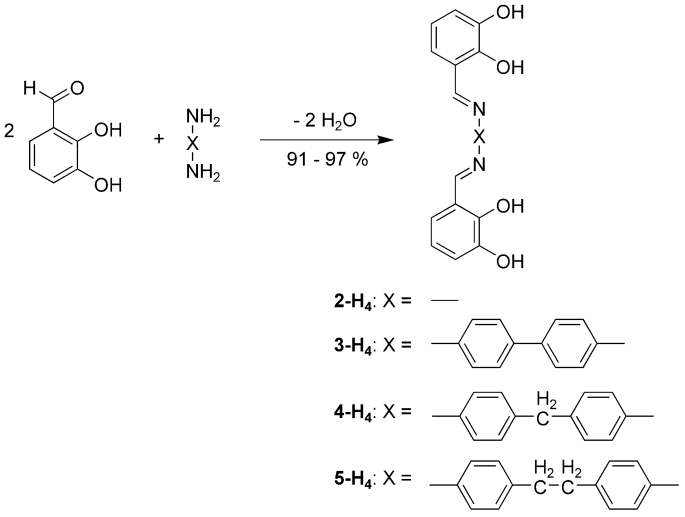


Figure 2. Schematic representation of dicatechol ligands possessing rigid connectors and small central stereo-controlling alkyl units.

investigate if long-range stereochemical information transfer between two connected complex units can occur in systems with long "semirigid" ligands.

Results

Ligand synthesis: The bisimine-bridged dicatechol ligands **2-H$_4$**–**5-H$_4$** are easily prepared by condensation of appropriate diamines with two equivalents of 2,3-dihydroxybenzaldehyde (Scheme 1).[66] The preparation and characterization of

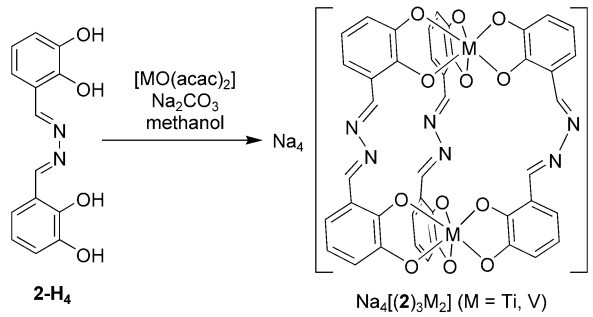


Scheme 1. Synthesis of the bisimine-bridged dicatechol ligands **2-H$_4$**–**5-H$_4$**.

2-H$_4$ was described earlier.[64] The ligand **2-H$_4$** possesses a rigid (but short) spacer connecting the ligand units. In the benzidine derivative **3-H$_4$** the two ligand units are also bridged by a rigid spacer. In **4-H$_4$** and **5-H$_4$** rigid linear connectors on the one side are attached to the ligand moieties, and, on the other side, are bound to a flexible central stereo-controlling unit: either -CH_2- (**4-H$_4$**) or -CH_2CH_2- (**5-H$_4$**). The ligands **3-H$_4$**–**5-H$_4$** are obtained in 91 to 97% yield and are characterized by standard methods (^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis). As a characteristic ^{1}H NMR signal, the resonance of the imine proton of the ligands in [D$_6$]DMSO appears at $\delta = 8.9$–9.0 ppm.

Formation and structure of Na$_4$[(2)$_3$V$_2$]: Titanium(IV) and vanadium(IV) complexes of ligand **2-H$_4$** can be easily prepared by simple mixing of **2-H$_4$** with the alkali metal carbonate and [MO(acac)$_2$] (M = Ti, V; acac = acetylacetonate) in methanol (Scheme 2). After the mixture is stirred overnight, the solvent is removed and the obtained solids are purified by chromatography on lipophilic Sephadex LH20.[64]

The titanium(IV) complex Na$_4$[(**2**)$_3$Ti$_2$] was already reported by us. The complex shows a helicate structure with two equal configured complex units. A sodium cation can be observed in the interior of the helicates in the solid state, and



Scheme 2. Synthesis of Ti^{IV} and V^{IV} complexes of ligand **2-H$_4$**.

NMR spectroscopy indicates that this binding takes place in solution as well.[64]

The vanadium(IV) complex Na$_4$[(**2**)$_3$V$_2$] was isolated in 92% yield and was characterized by elemental analysis and positive FAB mass spectrometry in 3-nitrobenzoic acid (3-NBA) as matrix. Characteristic peaks of the dinuclear coordination compound are detected at m/z 999 {Na$_4$[(**2**)$_3$V$_2$]H$^+$} and 977 {Na$_3$[(**2**)$_3$V$_2$]H$_2^+$}. X-ray–quality crystals of Na$_4$[(**2**)$_3$V$_2$]·5 MeOH·Et$_2$O were obtained by slow diffusion of diethyl ether into a methanolic solution of Na$_4$[(**2**)$_3$V$_2$]. The compound crystallizes in the monoclinic space group $C2/c$ (no. 15), with cell parameters $a = 13.905(1)$, $b = 18.387(1)$, $c = 21.368(1)$ Å, and $\beta = 90.84(1)°$. The structure was refined to $R = 0.074$.

Figure 3a shows the dinuclear tetraanionic helicate [(**2**)$_3$V$_2$]$^{4-}$, with the three azine-bridged dicatechol ligands **2** wrapping around the two vanadium(IV) centers (Figure 3b).

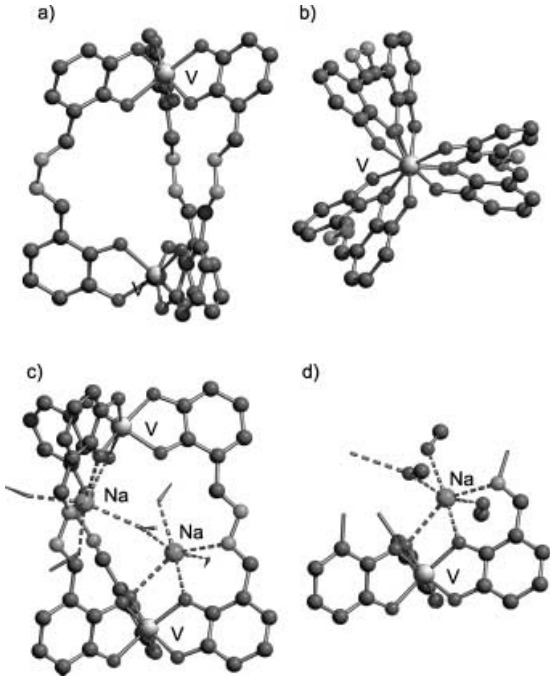
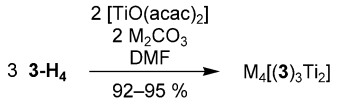


Figure 3. Part of the solid state structure of Na$_4$[(**2**)$_3$V$_2$]·5 MeOH·Et$_2$O. Hydrogen atoms are omitted for clarity and methanol is only indicated. a) Side view of the dinuclear triple-stranded helicate [(**2**)$_3$V$_2$]$^{4-}$; b) top view of the dinuclear triple-stranded helicate [(**2**)$_3$V$_2$]$^{4-}$; c) [(**2**)$_3$V$_2$]$^{4-}$ with encapsulated sodium cations and methanol molecules; d) representation, showing the coordination at the encapsulated sodium cations.

Two different conformations are observed at the azine bridges. One of the spacers of **2** adopts an s-*cis* orientation at the N–N unit (dihedral angle at C=N–N=C 48.8°), with the nitrogen lone pairs pointing away from the cavity of the helicate and the imine hydrogen atoms pointing inwards. The other two spacers adopt an s-*trans* conformation (C=N–N=C –155.9°), with one lone pair of one nitrogen atom pointing outwards and the other inwards. The latter conformation is enforced by encapsulation of two sodium ions in the interior of the helicate $[(\mathbf{2})_3V_2]^{4-}$ (Figure 3c). Each of the Na^+ ions binds to two internal catecholate oxygen atoms of a complex moiety and to one of the internal N atoms. Additionally, two methanol ligands bind to each of the sodium cations, and a further methanol group bridges the two cations (Figure 3d).

The coordination chemistry at the vanadium centers of $[(\mathbf{2})_3V_2]^{4-}$ can be described as distorted octahedral with a V···V separation of 8.339 Å within the complex. The helicate, with the same configuration at both metal-complex units, is the favored diastereoisomer due to the rigidity of the linear conjugated spacer.[28,52,61,67,68]

Formation and structure of $M_4[(\mathbf{3})_3Ti_2]$ (M = Li, Na, K): Titanium(IV) complexes of ligand **3** cannot be prepared as was described for the corresponding complexes of ligand **2** due to the low solubility of **3**. Therefore, **3-H$_4$**, $[TiO(acac)_2]$, and the corresponding alkali metal carbonate are dissolved in DMF (Scheme 3). Within minutes the solution turns orange-red and is then stirred overnight at room temperature. Volatile components are removed under vacuum to obtain the complex salts $M_4[(\mathbf{3})_3Ti_2]$ (M = Li, Na, K) as red solids in 92–95% yield.



Scheme 3. Synthesis of $M_4[(\mathbf{3})_3Ti_2]$ complexes.

The dinuclear complexes were characterized by elemental analysis. Positive FAB MS (3-NBA) reveals characteristic peaks at *m*/*z* 1379 $\{H_2Li_3[(\mathbf{3})_3Ti_2]^+\}$ and 1385 $\{HLi_4[(\mathbf{3})_3Ti_2]^+\}$, and 1427 $\{H_2Na_3[(\mathbf{3})_3Ti_2]^+\}$ and 1449 $\{HNa_4[(\mathbf{3})_3Ti_2]^+\}$, or 1475 $\{H_2K_3[(\mathbf{3})_3Ti_2]^+\}$ and 1513 $\{HK_4[(\mathbf{3})_3Ti_2]^+\}$, respectively. Upon complex formation, the imine proton, which appears in the ^{1}H NMR of **3-H$_4$** in [D$_6$]DMSO at $\delta = 9.01$ ppm, is shifted upfield to $\delta = 8.69$–8.71 ppm. The signals of the spacer are observed as two doublets at $\delta = 7.57/7.19$ (M = Li, J = 7.1 Hz), 7.56/7.21 (M = Na, J = 7.8 Hz), or 7.56/7.22 ppm (M = K, J = 7.1 Hz), while the catechol resonances are detected at $\delta =$ 7.04/6.41/6.21 (M = Li), 7.08/6.40/6.21 (M = Na), or 7.08/6.41/6.23 ppm (M = K). Thus, no significant differences are observed for the NMR shifts of different salts of $[(\mathbf{3})_3Ti_2]^{4-}$.[69]

X-ray quality crystals of $Na_4[(\mathbf{3})_3Ti_2]\cdot 13$ DMF were obtained by slow diffusion of diethyl ether into a solution of the sodium salt in DMF. The compound crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with the cell parameters $a = 22.716(1)$, $b = 24.487(1)$, $c = 22.868(1)$ Å and $\beta =$ 104.35°. The linear rigid ligands form a triple-stranded helicate $[(\mathbf{3})_3Ti_2]^{4-}$ with two similar-configured titanium(IV) complex units. The transition metals are fixed at a distance of Ti···Ti = 16.946 Å (Figure 4). The total length of the cylindrical complex is approximately 2.1 nm.[13]

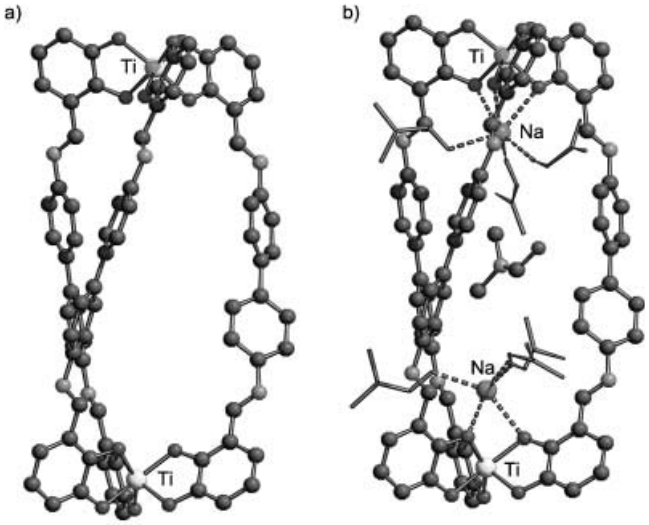


Figure 4. a) View of the dinuclear triple-stranded helicate $[(\mathbf{3})_3Ti_2]^{4-}$ in the solid state; b) structure of $[(\mathbf{3})_3Ti_2]^{4-}$ including encapsulated sodium cations and DMF molecules. Hydrogen atoms are omitted for clarity, and DMF molecules, which are coordinated to sodium cations, are only shown schematically.

The ligands (**3**) slightly wrap around the metals and adopt a conformation with the imine hydrogen atoms pointing into the cavity, directed towards the catecholate oxygen atoms. This orientation leads to the upfield shift of the resonance of this proton in the ^{1}H NMR spectra. The bridging biaryl units are twisted by 33.0, 21.6, and 45.1°, respectively. In the solid state, two sodium cations are bound in the interior of the helicate, each binding to the internal catecholate oxygen atoms and to three DMF molecules. An additional DMF molecule is encapsulated in the center of the cavity (Figure 4b).

Formation and structure of $M_4[(\mathbf{4})_3Ti_2]$ (M = Li, Na, K): Reaction of titanium(IV) ions with ligand **4-H$_4$** in the presence of the corresponding alkali metal carbonate in DMF leads to the assembly of dinuclear complexes $M_4[(\mathbf{4})_3Ti_2]$ in quantitative yield (Scheme 4).

Scheme 4. Synthesis of $M_4[(\mathbf{4})_3Ti_2]$ and $M_4[(\mathbf{5})_3Ti_2]$ complexes.

The complexes $M_4[(\mathbf{4})_3Ti_2]$ were characterized by elemental analysis, FAB MS, and NMR spectroscopy. For example, in the positive FAB mass spectrum of $Li_4[(\mathbf{4})_3Ti_2]$ characteristic peaks can be detected at *m*/*z* 1415 $\{H_3Li_2[(\mathbf{4})_3Ti_2]\}^+$ and

1421 $\{H_2Li_3[(\mathbf{4})_3Ti_2]\}^+$. A corresponding peak for the anion $\{Li_3[(\mathbf{4})_3Ti_2]\}^-$ appears in the negative FAB mass spectrum at *m/z* 1419. The lithium salt $Li_4[(\mathbf{4})_3Ti_2]$ in [D$_6$]DMSO shows peaks in the ^{1}H NMR spectrum at $\delta = 8.75$ (6H, imine), 7.14 (br., 24H; spacer-aryl), 7.05 (dd, $J = 8.0$, 1.4 Hz, 6H; cat), 6.35 (t, $J = 8.0$ Hz, 6H; cat), and 6.11 ppm (dd, $J = 8.0$, 1.4 Hz, 6H; cat). The corresponding aromatic and imine ^{1}H NMR resonances of the potassium or the sodium salt show no significant shift differences compared to the lithium compound. The signal of the spacer methylene unit, however, appears for both the potassium and the sodium salts as a singlet at $\delta = 3.87$ ppm. In the case of $Li_4[(\mathbf{4})_3Ti_2]$ two separate signals are observed at $\delta = 3.86$ and 3.84 ppm for the CH_2 group.[70]

We were able to obtain crystals of $Na_4[(\mathbf{4})_3Ti_2]\cdot 10$ DMF by diffusion of diethyl ether into a DMF solution. The complex crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with cell parameters $a = 25.887(1)$, $b = 12.584(1)$, $c = 34.210(1)$ Å, $\beta = 96.45(1)°$ and was refined to $R = 0.122$. Ligand **4** with a central CH_2 unit leads to the formation of the triple-stranded *meso*-helicate $[(\mathbf{4})_3Ti_2]^{4-}$. The solid-state structure shows the "C"-shaped conformation at the ligands (**4**), which leads to different configurations at the two complex units (Figure 5a).[45] The *meso*-helicate $[(\mathbf{4})_3Ti_2]^{4-}$ is as was described for $M_4[(\mathbf{4})_3Ti_2]$. Elemental analyses showed the correct composition for the compounds, and characteristic peaks were observed in the positive (e. g.: *m/z* 1463 $\{H_2Li_2[(\mathbf{5})_3Ti_2]\}^+$) as well as in the negative FAB mass spectra (e. g.: *m/z* 1455 $\{HLi_2[(\mathbf{5})_3Ti_2]\}^-$ and 1461 $\{Li_3[(\mathbf{5})_3Ti_2]\}^-$). ^{1}H NMR spectroscopy in [D$_6$]DMSO reveals the resonances of the imine proton at $\delta = 8.67$ (M = Li), 8.80 (M = Na), and 8.74 ppm (M = K), of the spacer at $\delta = 7.29/7.10/2.80$ (M = Li), 7.32/7.18/2.81 (M = Na), and 7.33/7.19/2.82 ppm (M = K), and of the catecholate units at $\delta = 7.03/6.36/6.14$ (Li), 7.08/6.38/6.18 (Na), and 7.07/6.37/6.17 ppm (K). Again, no significant differences were observed comparing the spectra of the complex salts $M_4[(\mathbf{5})_3Ti_2]$ with different cations M^+.

Crystals of $Na_4[(\mathbf{5})_3Ti_2]\cdot 13$ DMF$\cdot H_2O$ were obtained from wet DMF/diethyl ether. The complex crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with cell parameters $a = 24.870(1)$, $b = 23.601(1)$, $c = 23.564(1)$ Å, $\beta = 104.85(1)°$ and was refined to $R = 0.102$.

The three **5** ligands, with an ethylene moiety as central unit, wrap slightly around the two metal centers, leading to the same configuration at the two metal-complex units. The obtained supramolecular "cylinder" is 2.25 nm long with a Ti···Ti separation of 1.9060 nm (Figure 6a). Two sodium cati-

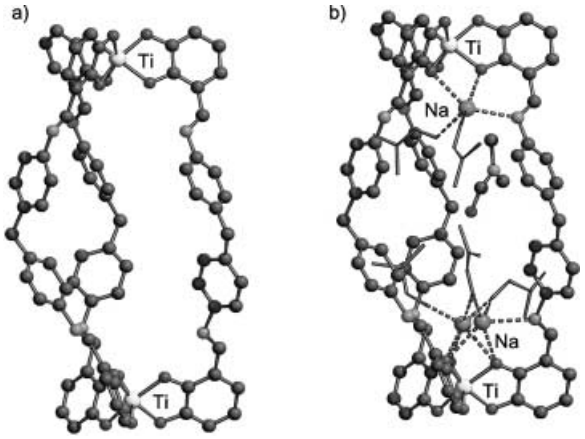


Figure 5. a) View of the dinuclear triple-stranded *meso*-helicate $[(\mathbf{4})_3Ti_2]^{4-}$ in the solid state; b) structure of $[(\mathbf{4})_3Ti_2]^{4-}$ including encapsulated sodium cations and DMF molecules. Hydrogen atoms are omitted for clarity, and DMF molecules, which are coordinated to sodium cations, are only shown schematically.

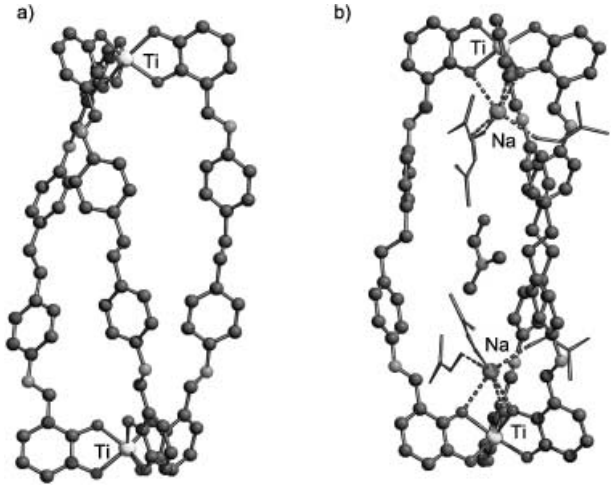


Figure 6. a) View of the dinuclear triple-stranded helicate $[(\mathbf{5})_3Ti_2]^{4-}$ in the solid state; b) structure of $[(\mathbf{5})_3Ti_2]^{4-}$ including encapsulated sodium cations, and DMF molecules. Hydrogen atoms are omitted for clarity, and DMF molecules, which are coordinated to sodium cations, are only shown schematically.

2.05 nm long, and the metals (Ti···Ti) are 1.6845 nm apart. Again, two sodium cations are encapsulated in the interior of the complex. One of the cations shows a disorder over two positions (Figure 5b). In addition to the interaction with two internal catecholate oxygen atoms and two or three DMF molecules, respectively, the cations bind to the imine nitrogen atoms of one of the three **4** ligands, enforcing an "inward" orientation of the imines of this strand. Na–N distances are 2.58–2.59 Å. One additional DMF molecule is located in the inner cavity of the complex.

Formation and structure of $M_4[(\mathbf{5})_3Ti_2]$ (M = Li, Na, K): The complex salts $M_4[(\mathbf{5})_3Ti_2]$ are prepared in quantitative yield ons are encapsulated in the interior of the helicate, each binding to three internal catecholate oxygen atoms and to three DMF molecules. One molecule of DMF fills the internal space of the cavity (Figure 6b).

Temperature-dependent NMR investigations on $Na_4[(\mathbf{4})_3Ti_2]$ and $Na_4[(\mathbf{5})_3Ti_2]$: For dinuclear helicate-type complexes with an odd number of CH_2 units in the spacer, NMR spectroscopy is a powerful tool to distinguish between the helicate and the *meso*-helicate form.[27,42,44,45,71,72]

Figure 7 shows schematic representations of the situation that is found for methylene or ethylene spacers either in hel-

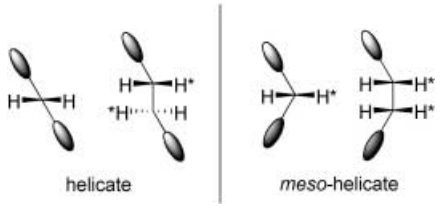


Figure 7. Schematic representation of the orientation of ligands with methylene or ethylene spacers in the helicate and *meso*-helicate. Homotopic and diastereotopic protons are indicated.

icate or *meso*-helicate structures. In the case of the ethylene spacer we expect two sets of signals for the helicate as well as for the *meso*-helicate. However, in the case of the methylene linkage, only one signal is expected for the helicate, whereas two diastereotopic protons are present for the *meso*-helicate. Therefore, we would expect two signals for the methylene unit of the *meso*-helicate $[(\mathbf{4})_3Ti_2]^{4-}$.[42,44,45,72] This is only observed for the lithium salt $Li_4[(\mathbf{4})_3Ti_2]$ which shows, in [D_6]DMSO at room temperature (400 MHz), two signals at $\delta = 3.86$ and 3.84 ppm for the spacer. Under the same conditions singlets are observed for the alkyl units of the potassium as well as of the sodium salt. This is attributed to a low inversion barrier for the complex units,[73] which depends on the internally bound counterions.[44] Therefore we investigated the spectra of $Na_4[(\mathbf{4})_3Ti_2]$ at low temperature.

The ^{1}H NMR spectrum of $Na_4[(\mathbf{4})_3Ti_2]$ in [D_4]methanol at room temperature shows only one singlet at $\delta = 3.90$ ppm for the protons of the central methylene unit. Upon cooling of the NMR sample, the signal of the CH_2 group broadens and starts to split. At 233 K two separate doublets are observed at $\delta = 3.86$ and 3.93 ppm ($J = 15$ Hz) (Figure 8a), revealing that the *meso*-helicate $Na_4[(\mathbf{4})_3Ti_2]$ is present in solution as it is observed in the solid state. From the coalescence temperature (ca. 275 K) an energy barrier of $\Delta G^{\neq} = 57\ kJ\,mol^{-1}$ is estimated[74] for the degenerated inversion of the *meso*-helicate ($\Lambda\Lambda \rightarrow \Delta\Delta$).[44]

In the case of $Na_4[(\mathbf{5})_3Ti_2]$ a fast racemization reaction $\Lambda\Lambda \rightarrow \Delta\Delta$ and vice versa is expected to occur.[56] Unfortunately $Na_4[(\mathbf{5})_3Ti_2]$ is only slightly soluble in [D_4]methanol. We therefore had to perform the temperature-dependent NMR investigations in [D_7]DMF. Rather different results were obtained for the two complexes $Na_4[(\mathbf{4})_3Ti_2]$ and $Na_4[(\mathbf{5})_3Ti_2]$ in this solvent.

The ^{1}H NMR spectrum of $Na_4[(\mathbf{4})_3Ti_2]$ in [D_7]DMF at 500 MHz shows broad signals at room temperature for the methylene protons. At high temperature (Figure 8b) a sharp singlet can be detected for this group at $\delta = 4.07$ ppm (350 K). Coalescence occurs at approximately 305 K. At low temperature (253 K) two separate doublets can be observed for the diastereotopic protons at $\delta = 4.22$ and 3.94 ppm ($J = 13.4$ Hz). This shows the presence of the *meso*-helicate in solution. According to NMR spectroscopy no significant amounts of the chiral helicate were present. A barrier of $\Delta G^{\neq} = 59\ kJ\,mol^{-1}$ can be estimated[74] for the inversion of the complex, which is in accordance with the corresponding results obtained in [D_4]methanol.

The racemization barrier of $Na_4[(\mathbf{5})_3Ti_2]$ is rather low. We could therefore not freeze out the inversion process in the

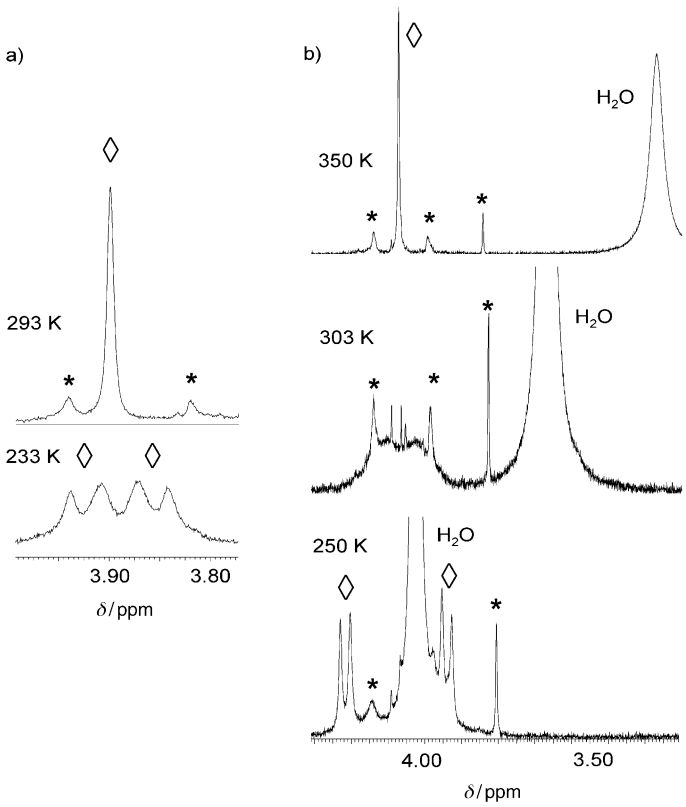


Figure 8. Temperature-dependent NMR spectra of $Na_4[(\mathbf{4})_3Ti_2]$ in [D_4]methanol (a) or [D_7]DMF (b) showing the splitting of the signal of the CH_2 group (◇) into two doublets at low temperature (*: impurities).

NMR spectrum in [D_7]DMF at 500 MHz. However, at 190 K the signal of the alkyl unit ($\delta = 3.05$ ppm at room temperature) broadens significantly, indicating that this temperature is close to the coalescence temperature. At lower temperature the sample solidifies. Therefore the barrier for the racemization of $Na_4[(\mathbf{5})_3Ti_2]$ can be estimated to be $\Delta G^{\neq} < 32\ kJ\,mol^{-1}$.[74] Our NMR investigations in [D_7]DMF at 500 MHz show that the barrier for the inversion of the *meso*-helicate $Na_4[(\mathbf{4})_3Ti_2]$ is approximately twice as high as that of the helicate $Na_4[(\mathbf{5})_3Ti_2]$.

Discussion

Herein we describe a series of bisimine-bridged dicatechol ligands **2-H$_4$**–**5-H$_4$** which form dinuclear triple-stranded complexes in self-assembly processes with surprisingly high diastereoselectivity. All ligands are rigid[75] with some degree of flexibility introduced into ligands **4-H$_4$** and **5-H$_4$**. To understand the structure of the ligands in the complexes we have to consider conformational restrictions in the ligand strands based on dipole–dipole interactions, conjugation, and cation complexation.

Conformational considerations: Figure 9a shows different orientations that can be adopted by the imine units of ligands **2**–**5**. Conformation **A** represents a favored orientation. Here the imine group is oriented away from the inter-

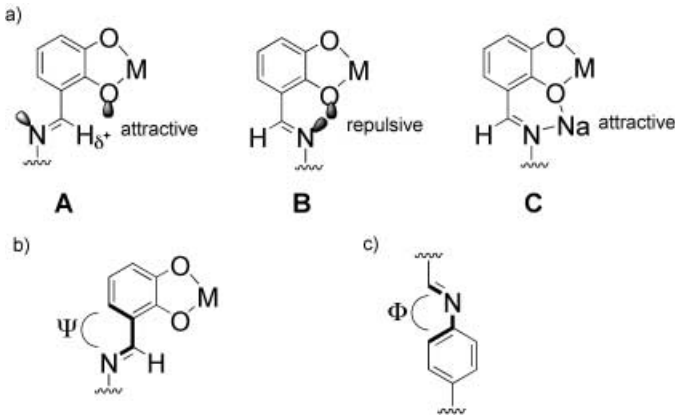


Figure 9. a) Schematic representation of the imine orientations and of the dihedral angles Ψ (b) and Φ (c).

nal catecholate oxygen atom and an attractive dipole–dipole interaction occurs between the imine proton and the lone pair of the oxygen atom. In **B** a disfavored conformation is shown in which a repulsive interaction takes place between the nitrogen and oxygen lone pair. However, structure **C** can be adopted if a cation binds to the internal catecholate oxygen atom as well as to the imine nitrogen atoms, and thus compensates for the charge of the electron pairs. In the presented X-ray structures of $Na_4[(\mathbf{2}–\mathbf{5})_3(V/Ti)_2]$, the imine group usually is in conjugation with the catechol. This leads to small dihedral angles $\Psi = 0.18–15°$ (Figure 9b) in the case of a structure like **A**. If a cation coordinates (**C**), Ψ becomes approximately 175°. On the other hand, the imine is not in conjugation with the aromatic ring of the spacer (Figure 9c), and the dihedral angle Φ varies from 13° to 49°. However, this dihedral angle Φ does not influence the linearity of the spacer, due to the *para* substitution at the phenyl group.

Stereochemical considerations: It is not a surprise that the rigid linear ligands **2-H$_4$** and **3-H$_4$** form helicates.[68,69,75] The linear ligand transfers the stereochemical information directly from one complex unit to the other. To obtain a *meso*-helicate, the ligand has to bend, that is, to adopt a "C"-type shape. Due to the buildup of strain, this is highly disfavored.

In the case of the ligand **5-H$_4$**, which contains a central ethylene linkage, it is also understandable that the helicate is favored over the *meso* form because of symmetry arguments. In the favored zigzag conformation **D** (Figure 10),

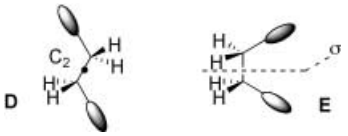


Figure 10. Different conformations of an ethylene unit, which have to be adopted in a helicate (**D**) or a *meso*-helicate (**E**).

the ethylene linkage does not possess the mirror plane that is necessary for the *meso*-helicate. To form the *meso*-helicate, the ethylene linkage has to adopt the sterically disfavored staggered conformation **E**. Minimization of strain energy leads to the preferred formation of the homochiral helicate if ligand **5** is used.[56]

The most surprising result is obtained with ligand **4-H$_4$**, which forms the achiral *meso*-helicate $[(\mathbf{4})_3Ti_2]^{4-}$ with high diastereoselectivity. As indicated in Figure 11, ligand **4** can

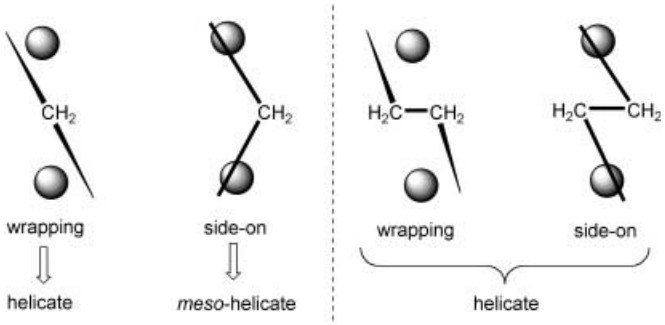
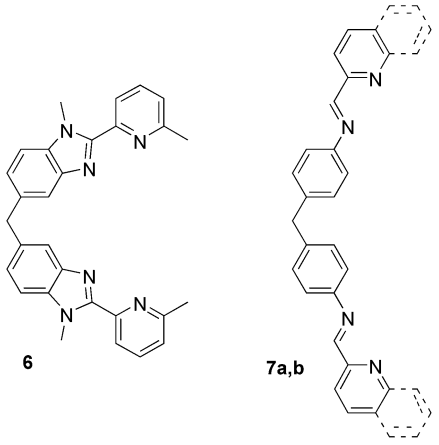


Figure 11. Schematic representation of the possible conformations of ligand **4** and **5** to either wrap around the two metals or to bind by side-on coordination. Hereby ligand **4** forms the helicate by "wrapping", whereas "side-on" coordination results in the *meso*-helicate. With ligand **5** the homochiral helicate is formed in all cases.

adopt two different conformations, "side-on" and "wrapping", in which either the C_2 axis of the helicate ("wrapping")[38,76] or the mirror plane of the *meso*-helicate ("side-on")[31,43] is present. Thus, ligand **4** is in principle able to form both the chiral helicate and the achiral *meso*-helicate.

For the small ligand **1a**, the same arguments can be used. However, in contrast to **4**, **1a** has only a very short spacer. Thus it is not able to wrap around the metal centers, but has to approach side-on with both ligand units from the same face of the dinuclear complex. Ligand **1a** forms the *meso*-helicate $[(\mathbf{1a})_3Ti_2]^{4-}$ with high diastereoselectivity.[31] The spacer of **4** is much longer than that of **1a**, and therefore it is surprising that here the *meso*-helicate Λ,Δ-$[(\mathbf{4})_3Ti_2]^{4-}$ is also formed with high stereoselectivity.

Furthermore, Williams,[77,78] Hannon,[58,60] and Yoshida[62,63] and their respective co-workers already introduced the methylene-bridged ligands **6** and **7**, which form the triple-stranded homochiral helicates $[(\mathbf{6})_3Co_2]^{4+}$[77] and $[(\mathbf{7a})_3Ni_2]^{4+}$[58] or $[(\mathbf{7a})_3Zn_2]^{4+}$[62,63] with high diastereoselectivity.



NMR investigation of the diamagnetic triple-stranded helicate $[(\mathbf{7a})_3Fe_2]^{4+}$ shows that this chiral complex is formed in a highly diastereoselective way.[58,60] The corresponding dinuclear zinc complex $[(\mathbf{7a})_3Zn_2]^{4+}$ leads to a complicated NMR spectrum at low temperature, which is attributed to restricted rotation of the phenyl groups and eventually to some ligand dissociation.[62,63] For the double-stranded complex $[(\mathbf{7b})_2Ag_2]^{2+}$, NMR spectroscopy shows signals of both diastereomeric forms, that is, the helicate and the *meso*-helicate.[60]

Both ligands **4** and **7** possess a similar geometric arrangement but, in coordination studies, led to different diastereoisomers with high selectivity. At first sight this seems to be surprising. To explain this contradiction we have to speculate: In the case of **7**, the imine groups are a part of the metal-binding unit. The flexibility of the ligand is thus reduced, leading to a state of high preorganization which facilitates wrapping around the metals.[58,62] To form dinuclear triple-stranded complexes, the metal-complex units have to adopt a well-defined geometry. To minimize distortion at the metal center, the ligand **7** wraps around the metal centers and the helical complex $[(\mathbf{7})_3M_2]^{4+}$ is formed. Here constraints at the metal center as well as at the ligand control the structure. On the other hand, ligand **4** shows a higher flexibility than **6** or **7** due to some rotational freedom at the imine units. Therefore, constraints, which accumulate upon complex formation, can be cancelled by dihedral distortion of those units.

"Side-on" binding of the ligands is observed in the solid state for complex $[(\mathbf{4})_3Ti_2]^{4-}$ and $[(\mathbf{5})_3Ti_2]^{4-}$, as well as in solution for ligand **4**. We can speculate that the side-on coordination might be entropically favored. If the ligand wraps around the metal centers, the inversion of the metal centers is disfavored, due to a major structural rearrangement of the complex during this process. In the side-on coordination the complexes are highly dynamic. This coordination should therefore be entropically favored because the system can adopt a state of "higher disorder".

A shallow potential surface for the racemization of helicates was demonstrated before for related small triple-stranded helicates by Raymond et al.[28] and later by us.[72] In the dynamic systems $Na_4[(\mathbf{4})_3Ti_2]$ and $Na_4[(\mathbf{5})_3Ti_2]$, a dramatic difference can be detected for the inversion barriers of $\Delta G^{\ddagger} = 59\ kJ\,mol^{-1}$ ($Na_4[(\mathbf{4})_3Ti_2]$) and $\Delta G^{\ddagger} < 32\ kJ\,mol^{-1}$ ($Na_4[(\mathbf{5})_3Ti_2]$). This indicates that inversion proceeds by different mechanisms (Figure 12).

For the ethylene-linked system $Na_4[(\mathbf{5})_3Ti_2]$, the inversion proceeds by successive racemization of the single complex units. Hereby the *meso* compound is formed as a "high-energy" intermediate in which the ethylene linkage adopts the unfavored staggered conformation. For $Na_4[(\mathbf{4})_3Ti_2]$ the simultaneous inversion of the two complex units is assumed. In the transition state both titanium(IV) complex units possess a trigonal-prismatic coordination geometry.[73] Due to the racemization of both units at once, the barrier for this process is approximately twice as high as for the successive inversion of the two units in $Na_4[(\mathbf{5})_3Ti_2]$. This can be observed by NMR spectroscopy and is probably due to a mechanical coupling of the binding sites in the more rigid ligand **4**. Ligand **5**, on the other hand, possesses higher flexibility.

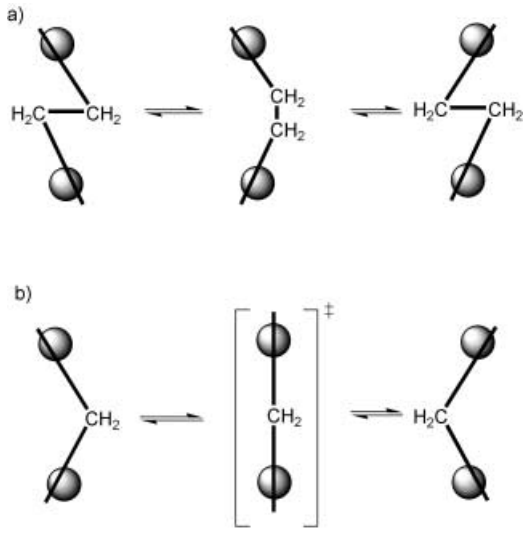


Figure 12. Schematic representation of a) the stepwise racemization of the helicate $Na_4[(\mathbf{5})_3Ti_2]$ and b) simultaneous inversion of the complex units of the *meso*-helicate $Na_4[(\mathbf{4})_3Ti_2]$.

In $Na_4[(\mathbf{4})_3Ti_2]$ the achiral ("trigonal-prismatic") transition-state geometry seems to be energetically favored over the chiral intermediate in which the ligand wraps around the metal.

Conclusion

In this study we investigated the coordination chemistry of a series of bisimine-bridged dicatechol ligands and found a surprising long-range transfer of stereochemical information in the obtained helicate-type complexes. With ligands **4** and **5**, a rigid connector transfers the stereochemical information of the first complex unit to a stereo-controlling unit that is located at a distance of about 1 nm from the complex moiety. This small central unit influences the stereochemistry at the second titanium(IV) triscatecholate complex, which again is located 1 nm away. Thus, the stereochemical information is transferred over a distance of nearly 2 nm. If the stereo-controlling unit consists of a methylene group, the heterochiral *meso*-helicate is formed, while a direct rigid connection or the presence of an ethylene group leads to the homochiral helicate.

In summary, we demonstrated that the three-dimensional structure of nanometer-sized supramolecular aggregates can be controlled by very small units. Appropriate rigid moieties have to be present as stereochemical communicators that are able to transfer the chiral information over long distances. It is crucial to observe and to rationalize factors that influence the stereochemistry at such "small" supramolecular aggregates like the helicates to learn how to rationally design bigger structures.[79]

Experimental Section

NMR spectra were recorded on a Bruker DRX 500, WM 400 or a Varian Inova 400 or Unity 500 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. UV/Vis spectra were obtained with a Perkin Elmer Lambda2 Spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyzer. Melting points: Büchi B-540 (uncorrected). Ligand **2-H$_4$** was prepared as described before.[64]

Data sets were collected on a Nonius KappaCCD diffractometer, equipped with a Nonius FR591 rotating-anode generator. Programs used: data collection: COLLECT (Nonius B.V., 1998); data reduction: Denzo-SMN;[80] absorption correction: SORTAV;[81] structure solution: SHELXS-97;[82] structure refinement: SHELXL-97 (G.M. Sheldrick, University of Göttingen, **1997**); graphics: SCHAKAL (E. Keller, University of Freiburg, **1997**); and XP (Bruker AXS, 2001).

CCDC-200000, -200001, -200002, and -205260 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

General procedure for the preparation of the ligands: 2,3-Dihydroxybenzaldehyde (2 mmol) and the appropriate diamine (1 mmol) were dissolved in methanol (20 mL). After a few minutes an orange material precipitated which, after being left to stand overnight, was isolated by filtration and dried in vacuum.

Ligand 3-H$_4$: Yield: 97% of a red solid; m.p. 275°C (decomp); ^{1}H NMR ([D$_6$]DMSO): δ = 9.01 (s, 2H), 7.83 (d, J = 8.3 Hz, 4H), 7.54 (d, J = 8.3 Hz, 4H), 7.13 (d, J = 7.7 Hz, 2H), 6.96 (d, J = 7.7 Hz, 2H), 6.81 ppm (pseudo t, J = 7.7 Hz, 2H); ^{13}C NMR ([D$_6$]DMSO): δ = 165.2 (CH), 149.9 (C), 147.5 (C), 146.1 (C), 138.3 (C), 128.0 (CH), 123.3 (CH), 122.5 (CH), 119.9 (C), 119.5 (CH), 119.3 ppm (CH); IR (KBr): $\tilde{\nu}$ = 3438, 1624, 1579, 1460, 1368, 1277, 1215, 829, 735 cm^{-1}; MS (EI, 70 eV): m/z: 424 (100%) $[M]^+$. HRMS calcd for $C_{26}H_{20}N_2O_4$: 424.1423, found: 424.1432; elemental analysis calcd (%) for $C_{26}H_{20}N_2O_4$: C 73.57, H 4.75, N 6.60; found: C 73.57, H 4.94, N 6.55.

Ligand 4-H$_4$: Yield: 91% of a red solid; m. p. 227°C (decomp); ^{1}H NMR ([D$_6$]DMSO): δ = 13.32 (br, 2H), 9.21 (br, 2H), 8.91 (s, 2H), 7.37 (d, J = 8.8 Hz, 4H), 7.34 (d, J = 8.8 Hz, 4H), 7.09 (dd, J = 7.7, 1.7 Hz, 2H), 6.96 (dd, J = 7.7, 1.7 Hz, 2H), 6.79 (t, J = 7.7 Hz, 2H), 4.02 ppm (s, 2H); ^{13}C NMR ([D$_6$]DMSO): δ = 163.9 (CH), 150.0 (C), 146.4 (C), 146.2 (C), 140.8 (C), 130.4 (CH), 123.4 (CH), 122.1 (CH), 120.0 (CH$_2$), 119.5 (CH), 119.4 ppm (CH); IR (KBr): $\tilde{\nu}$ = 3523, 3440, 3319, 1625, 1462, 1276, 1235, 733 cm^{-1}; MS (EI, 70 eV): m/z: 438 (100%) $[M]^+$; HRMS calcd for $C_{27}H_{22}N_2O_4$: 438.1580, found: 438.1579; elemental analysis calcd (%) for $C_{27}H_{22}N_2O_4$: C 73.96, H 5.06, N 6.39; found: C 73.74, H 5.11, N 6.24.

Ligand 5-H$_4$: Yield: 94% of a red solid; m. p. 231°C (decomp); ^{1}H NMR ([D$_6$]DMSO): δ = 13.38 (br, 2H), 9.21 (br, 2H), 8.92 (s, 2H), 7.35 (d, J = 8.5 Hz, 4H), 7.32 (d, J = 8.5 Hz, 4H), 7.10 (dd, J = 7.7, 1.7 Hz, 2H), 6.97 (dd, J = 7.7, 1.7 Hz, 2H), 6.80 (t, J = 7.7 Hz, 2H), 2.94 ppm (s, 4H); ^{13}C NMR ([D$_6$]DMSO): δ = 163.6 (CH), 150.0 (C), 146.2 (C), 146.1 (C), 141.0 (C), 130.1 (CH), 123.4 (CH), 121.8 (CH), 120.0 (CH$_2$), 119.5 (CH), 119.4 ppm (CH); IR (KBr): $\tilde{\nu}$ = 3429, 1623, 1463, 1274, 1228, 733 cm^{-1}; MS (EI, 70 eV): m/z: 452 (100%) $[M]^+$; HRMS calcd for $C_{28}H_{24}N_2O_4$: 452.1736, found: 452.1737; elemental analysis calcd (%) for $C_{28}H_{24}N_2O_4$: C 74.32, H 5.35, N 6.19; found: C 73.71, H 5.64, N 6.12.

Complex Na$_4$[(2)$_3$V$_2$]: Ligand **2-H$_4$** (150 mg, 0.55 mmol), Na_2CO_3 (39 mg, 0.37 mmol), and [VO(acac)$_2$] (97 mg, 0.37 mmol) were dissolved in methanol under argon. The dark mixture was stirred overnight, the solvent was removed under vacuum, and the residue was purified by chromatography over Sephadex LH20 (methanol). Yield: 92% of a black solid; IR (KBr) $\tilde{\nu}$ = 3409, 1619, 1439, 1329, 1262, 774, 739, 644 cm^{-1}; UV/Vis (methanol): λ = 195, 297, 570 nm. MS (pos. FAB, 3-NBA): m/z: 977 $[M-\mathrm{Na}+2\mathrm{H}]^+$, 999 $[M+\mathrm{H}]^+$; elemental analysis calcd (%) for $C_{42}H_{24}N_6Na_4O_{12}V_2\cdot 5H_2O$: C 46.34, H 3.15, N 7.72; found: C 46.41, H 3.57, N 7.18.

General procedure for the preparation of titanium(IV) complexes: Ligand (3 equiv), M_2CO_3 (M = Li, Na, K, 2 equiv), and [TiO(acac)$_2$] (1 equiv) were dissolved in DMF under argon. The orange mixture was stirred overnight and volatiles were removed in vacuum to obtain an orange-red material.

Complex Li$_4$[(3)$_3$Ti$_2$]: Yield: 92% of a red solid; ^{1}H NMR ([D$_6$]DMSO): δ = 8.69 (s, 6H), 7.57 (d, J = 7.4 Hz, 12H), 7.19 (d, J = 7.4 Hz, 12H), 7.04 (d, J = 7.1 Hz, 6H), 6.41 (pseudo t, J = 7.1 Hz, 6H), 6.21 ppm (d, J = 7.1 Hz, 6H); IR (KBr): $\tilde{\nu}$ = 3367, 3054, 2929, 2887, 1665, 1590, 1491, 1446, 1251, 740, 628 cm^{-1}; MS (pos. FAB, 3-NBA): m/z: 1379 $[M-\mathrm{Li}+2\mathrm{H}]^+$, 1385 $[M+\mathrm{H}]^+$; elemental analysis calcd (%) for $C_{78}H_{48}N_6Li_4O_{12}Ti_2\cdot 5H_2O\cdot 4$DMF: C 61.17, H 4.90, N 7.93; found: C 61.10, H 5.27, N 8.55.

Complex Na$_4$[(3)$_3$Ti$_2$]: Yield: 95% of a red solid; ^{1}H NMR ([D$_6$]DMSO): δ = 8.72 (s, 6H), 7.56 (d, J = 7.8 Hz, 12H), 7.21 (d, J = 7.8 Hz, 12H), 7.08 (d, J = 7.4 Hz, 6H), 6.40 (pseudo t, J = 7.4 Hz, 6H), 6.21 ppm (d, J = 7.4 Hz, 6H); IR (KBr): $\tilde{\nu}$ = 3419, 3027, 2866, 1667, 1588, 1490, 1449, 1412, 1248, 629 cm^{-1}; MS (pos. FAB, 3-NBA): m/z: 1383 $[M-3\mathrm{Na}+4\mathrm{H}]^+$, 1405 $[M-2\mathrm{Na}+3\mathrm{H}]^+$, 1427 $[M-\mathrm{Na}+2\mathrm{H}]^+$, 1449 $[M+\mathrm{H}]^+$; elemental analysis calcd (%) for $C_{78}H_{48}N_6Na_4O_{12}Ti_2\cdot 3H_2O\cdot 3$DMF: C 60.67, H 4.39, N 7.32; found: C 60.67, H 4.63, N 7.35.

Complex K$_4$[(3)$_3$Ti$_2$]: Yield: 93% of a red solid; ^{1}H NMR ([D$_6$]DMSO): δ = 8.69 (s, 6H), 7.56 (d, J = 7.1 Hz, 12H), 7.22 (d, J = 7.1 Hz, 12H), 7.08 (d, J = 7.0 Hz, 6H), 6.41 (pseudo t, J = 7.0 Hz, 6H), 6.23 ppm (d, J = 7.0 Hz, 6H); IR (KBr): $\tilde{\nu}$ = 3438, 3026, 2928, 2865, 1665, 1618, 1588, 1489, 1446, 1248, 1194, 627 cm^{-1}. MS (pos. FAB, 3-NBA): m/z: 1399 $[M-3\mathrm{K}+4\mathrm{H}]^+$, 1437 $[M-2\mathrm{K}+3\mathrm{H}]^+$, 1475 $[M-\mathrm{K}+2\mathrm{H}]^+$, 1513 $[M+\mathrm{H}]^+$; elemental analysis calcd (%) for $C_{78}H_{48}N_6K_4O_{12}Ti_2\cdot H_2O\cdot 4$DMF: C 59.27, H 4.31, N 7.68; found: C 59.06, H 4.53, N 7.11.

Complex Li$_4$[(4)$_3$Ti$_2$]: Yield: quantitative of a red solid; ^{1}H NMR ([D$_6$]DMSO): δ = 8.75 (s, 6H), 7.14 (br, 24H), 7.05 (dd, J = 8.0, 1.4 Hz, 6H), 6.35 (t, J = 8.0 Hz, 6H), 6.11 (dd, J = 8.0, 1.4 Hz, 6H), 3.86 (s, 3H), 3.84 ppm (s, 3H); IR (KBr): $\tilde{\nu}$ = 3408, 1666, 1617, 1591, 1502, 1446, 1386, 1252, 1193, 742, 657 cm^{-1}; MS (pos. FAB, 3-NBA): m/z: 1415 $[M-2\mathrm{Li}+3\mathrm{H}]^+$, 1421 $[M-\mathrm{Li}+2\mathrm{H}]^+$; (neg. FAB, 3-NBA): m/z: 1419 $[M-\mathrm{Li}]^-$; elemental analysis calcd (%) for $C_{81}H_{54}N_6Li_4O_{12}Ti_2\cdot 7H_2O\cdot 4$DMF: C 60.53, H 5.24, N 7.59; found: C 60.66, H 5.88, N 7.69.

Complex Na$_4$[(4)$_3$Ti$_2$]: Yield: quantitative of a red solid. ^{1}H NMR ([D$_6$]DMSO): δ = 8.77 (s, 6H), 7.16 (d, J = 8.8 Hz, 12H), 7.13 (d, J = 8.8 Hz, 12H), 7.07 (dd, J = 7.7, 1.4 Hz, 6H), 6.37 (t, J = 7.7 Hz, 6H), 6.14 (dd, J = 7.7, 1.4 Hz, 6H), 3.87 ppm (s, 6H); IR (KBr): $\tilde{\nu}$ = 1666, 1615, 1590, 1502, 1446, 1385, 1251, 1214, 742, 658 cm^{-1}; elemental analysis calcd (%) for $C_{81}H_{54}N_6Na_4O_{12}Ti_2\cdot 9H_2O\cdot 4$DMF: C 57.41, H 5.18, N 7.20; found: C 57.56, H 4.99, N 7.22.

Complex K$_4$[(4)$_3$Ti$_2$]: Yield: quantitative of a red solid; ^{1}H NMR ([D$_6$]DMSO): δ = 8.74 (s, 6H), 7.17 (d, J = 8.5 Hz, 12H), 7.13 (d, J = 8.5 Hz, 12H), 7.09 (dd, J = 8.0, 1.4 Hz, 6H), 6.36 (t, J = 8.0 Hz, 6H), 6.13 (dd, J = 8.0, 1.4 Hz, 6H), 3.86 ppm (s, 6H); IR (KBr): $\tilde{\nu}$ = 1665, 1616, 1589, 1444, 1386, 1252, 1214, 744, 657 cm^{-1}; MS (pos. FAB, 3-NBA): m/z: 1555 $[M+\mathrm{H}]^+$, 1517 $[M-\mathrm{K}+2\mathrm{H}]^+$; elemental analysis calcd (%) for $C_{81}H_{54}N_6K_4O_{12}Ti_2\cdot 9H_2O\cdot 4$DMF: C 55.57, H 5.01, N 6.97; found: C 56.00, H 5.33, N 6.82.

Complex Li$_4$[(5)$_3$Ti$_2$]: Yield: quantitative of a red solid. ^{1}H NMR ([D$_6$]DMSO): δ = 8.67 (s, 6H), 7.29 (d, J = 8.3 Hz, 12H), 7.10 (d, J = 8.3 Hz, 12H), 7.03 (dd, J = 7.7, 1.4 Hz, 6H), 6.36 (t, J = 7.7 Hz, 6H), 6.14 (d, J = 7.7 Hz, 6H), 2.80 ppm (s, 12H); IR (KBr): $\tilde{\nu}$ = 3429, 1664, 1619, 1592, 1445, 1251, 740 cm^{-1}; MS (pos. FAB, 3-NBA): m/z: 1463 $[M-\mathrm{Li}+2\mathrm{H}]^+$; (neg. FAB, 3-NBA): m/z: 1455 $[M-2\mathrm{Li}+\mathrm{H}]^-$, 1461 $[M-\mathrm{Li}]^-$; elemental analysis calcd (%) for $C_{84}H_{60}N_6Li_4O_{12}Ti_2\cdot 5H_2O\cdot 5$DMF: C 61.79, H 5.50, N 8.01; found: C 61.70, H 5.48, N 8.39.

Complex Na$_4$[(5)$_3$Ti$_2$]: Yield: quantitative of a red solid; ^{1}H NMR ([D$_6$]DMSO): δ = 8.80 (s, 6H), 7.32 (d, J = 8.3 Hz, 12H), 7.18 (d, J = 8.3 Hz, 12H), 7.08 (dd, J = 8.0, 1.4 Hz, 6H), 6.38 (t, J = 8.0 Hz, 6H), 6.18 (dd, J = 8.0, 1.4 Hz, 6H), 2.81 ppm (s, 12H); IR (KBr): $\tilde{\nu}$ = 1666, 1617, 1592, 1447, 1251, 740 cm^{-1}; MS (pos. FAB, 3-NBA): m/z: 1533 $[M+\mathrm{H}]^+$, 1511 $[M-\mathrm{Na}+2\mathrm{H}]^+$; elemental analysis calcd (%) for $C_{84}H_{60}N_6Na_4O_{12}Ti_2\cdot 3H_2O\cdot 4$DMF: C 61.35, H 5.04, N 7.45; found: C 61.67, H 5.71, N 7.20.

Complex K$_4$[(5)$_3$Ti$_2$]: Yield: quantitative of a red solid; ^{1}H NMR ([D$_6$]DMSO): δ = 8.74 (s, 6H), 7.33 (d, J = 8.5 Hz, 12H), 7.19 (d, J = 8.5 Hz, 12H), 7.07 (dd, J = 8.0, 1.4 Hz, 6H), 6.37 (t, J = 8.0 Hz, 6H), 6.17 (dd, J = 8.0, 1.4 Hz, 6H), 2.82 ppm (s, 12H); IR (KBr): $\tilde{\nu}$ = 1663, 1618, 1591, 1446, 1249, 740 cm^{-1}; elemental analysis calcd (%) for

$C_{84}H_{60}N_6K_4O_{12}Ti_2 \cdot 3H_2O \cdot 2DMF$: C 60.13, H 4.49, N 6.23; found: C 60.32, H 5.09, N 5.93.

X-ray crystal structure analysis of $Na_4[(2)_3V_2]$: formula $C_{42}H_{24}N_6O_{12}V_2Na_4 \cdot 5CH_3OH \cdot C_4H_{10}O$, $M_r = 1232.84$, black crystal $0.20 \times 0.10 \times 0.05$ mm, $a = 13.905(1)$, $b = 18.387(1)$, $c = 21.368(1)$ Å, $\beta = 90.84(1)°$, $V = 5462.6(6)$ Å^3, $\rho_{calcd} = 1.499$ g cm^{-3}, $\mu = 4.53$ cm^{-1}, empirical absorption correction ($0.915 \leq T \leq 0.978$), $Z = 4$, monoclinic, space group $C2/c$ (no. 15), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 11317 reflections collected ($\pm h$, $\pm k$, $\pm L$), $[(\sin\theta)/\lambda] = 0.66$ Å^{-3}, 6506 independent ($R_{int} = 0.047$) and 4624 observed reflections [$I \geq 2\sigma(I)$], 365 refined parameters, $R = 0.074$, $wR^2 = 0.185$, max. residual electron density 1.51 (-1.26) e Å^{-3} in the region of the diethyl ether molecule, this was refined with split positions, bond-length constraints, and common isotropic thermal-displacement parameters; hydrogen atoms at O41 and O51 from difference map; hydrogen atom at O61 could not be localized; others were calculated and all refined as riding atoms.

X-ray crystal structure analysis of $Na_4[(3)_3Ti_2]$: formula $C_{78}H_{48}N_6O_{12}Na_4Ti_2 \cdot 13C_3H_7NO$, $M_r = 2399.23$, red crystal $0.35 \times 0.10 \times 0.05$ mm, $a = 22.716(1)$, $b = 24.487(1)$, $c = 22.868(1)$ Å, $\beta = 104.35(1)°$, $V = 12323.4(9)$ Å^3, $\rho_{calcd} = 1.293$ g cm^{-3}, $\mu = 2.21$ cm^{-1}, empirical absorption correction ($0.927 \leq T \leq 0.989$), $Z = 4$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 80519 reflections collected ($\pm h$, $\pm k$, $\pm L$), $[(\sin\theta)/\lambda] = 0.59$ Å^{-1}, 21684 independent ($R_{int} = 0.093$) and 12768 observed reflections [$I \geq 2\sigma(I)$], 1137 refined parameters, $R = 0.138$, $wR^2 = 0.337$, max. residual electron density 2.25 (-1.11) e Å^{-3}, phenyl ring C85–C90 was fixed with restraints and refined with isotropic thermal parameters; nearly all of the DMF molecules are heavily disordered, therefore they were all refined with isotropic thermal parameters; hydrogen atoms were calculated and refined as riding atoms.

X-ray crystal structure analysis of $Na_4[(4)_3Ti_2]$: formula $C_{81}H_{54}N_6O_{12}Na_4Ti_2 \cdot 10C_3H_7NO$, $M_r = 2222.02$, red crystal $0.25 \times 0.20 \times 0.05$ mm, $a = 25.887(1)$, $b = 12.584(1)$, $c = 34.210(1)$ Å, $\beta = 96.45(1)°$, $V = 11073.8(10)$ Å^3, $\rho_{calc} = 1.333$ g cm^{-3}, $\mu = 2.37$ cm^{-1}, empirical absorption correction ($0.943 \leq T \leq 0.988$), $Z = 4$, monoclinic, space group $P2_1/n$ (no. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 27046 reflections collected ($\pm h$, $\pm k$, $\pm L$), $[(\sin\theta)/\lambda] = 0.54$ Å^{-1}, 14463 independent ($R_{int} = 0.068$) and 8074 observed reflections [$I \geq 2\sigma(I)$], 1228 refined parameters, $R = 0.122$, $wR^2 = 0.332$, max. residual electron density 1.94 (-0.82) e Å^{-3}, crystals only diffract to a relative low resolution, sodium atom Na6 was refined with split positions to a ratio of 0.56(2):0.44, phenyl ring C86–C91 was fixed with restraints; some of the DMF molecules are heavily disordered, therefore three of them were refined with isotropic thermal parameters, three other solvent DMF molecules were refined with one common isotropic thermal parameter per molecule, a non-disordered one was used as a model; hydrogen atoms were calculated and refined as riding atoms.

X-ray crystal structure analysis of $Na_4[(5)_3Ti_2]$: formula $C_{84}H_{60}N_6O_{12}Na_4Ti_2 \cdot 12C_3H_7NO \cdot 2/2C_3H_7NO \cdot H_2O$, $M_r = 2501.40$, orange crystal $0.40 \times 0.30 \times 0.10$ mm, $a = 24.870(1)$, $b = 23.601(1)$, $c = 23.564(1)$ Å, $\beta = 104.85(1)°$, $V = 13369.1(10)$ Å^3, $\rho_{calcd} = 1.243$ g cm^{-3}, $\mu = 2.07$ cm^{-1}, empirical absorption correction ($0.922 \leq T \leq 0.980$), $Z = 4$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 30735 reflections collected ($\pm h$, $\pm k$, $\pm L$), $[(\sin\theta)/\lambda] = 0.54$ Å^{-1}, 17329 independent ($R_{int} = 0.064$) and 9449 observed reflections [$I \geq 2\sigma(I)$], 1471 refined parameters, $R = 0.102$, $wR^2 = 0.282$, max. residual electron density 1.22 (-0.75) e Å^{-3}. Crystals only diffract to a relative low resolution; some of the DMF molecules are heavily disordered, therefore one out of the coordination sphere of the sodium atoms was refined with isotropic thermal parameters, the free solvent DMF molecules were refined with one common isotropic thermal parameter per molecule, a non-disordered one was used as a model; hydrogen atoms were calculated and refined as riding atoms; hydrogen atoms at the water could not be located.

[1] E. C. Constable, *Chem. Ind.* **1994**, 56–59

[2] a) J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**; b) J.-M. Lehn, *Angew. Chem.* **1990**, *102*, 1347–1362; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304–1319.

[3] a) J. S. Lindsey, *New J. Chem.* **1991**, *15*, 153–180; b) G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312–1319.

[4] a) D. Caulder, K. N. Raymond, *J. Chem. Soc. Dalton Trans.* **1999**, 1185–1200; b) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–907.

[5] J.-M. Lehn, *Chem. Eur. J.* **2000**, *6*, 2097–2102.

[6] B. J. Holliday, C. A. Mirkin, *Angew. Chem.* **2001**, *113*, 2076–2097; *Angew. Chem. Int. Ed.* **2001**, *40*, 2022–2042.

[7] a) V. Balzani, A. Credi, M. Venturi, *Chem. Eur. J.* **2002**, *8*, 5524–5532; b) D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242–1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154–1196.

[8] A. Werner, *Z. Anorg. Chem.* **1893**, *3*, 267.

[9] a) J.-M. Lehn, J.-P. Sauvage, J. Simon, R. Ziessel, *Nouv. J. Chim.* **1983**, *7*, 413–420; b) B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Angew. Chem.* **1996**, *108*, 1987–1990; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1838–1840; c) J.-M. Lehn, *Chem. Biol. (Introductory issue)* **1994**, xviii-xix; d) P. N. W. Baxter, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **2000**, *6*, 4510–4517; e) G. S. Hanan, C. R. Arana, J.-M. Lehn, D. Fenske, *Angew. Chem.* **1995**, *107*, 1191; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1122–1124; f) G. S. Hanan, C. R. Arana, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1996**, *2*, 1292–1302; g) D. P. Funeriu, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1997**, *3*, 99–104; h) P. N. W. Baxter, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 102–112; i) P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 113–120.

[10] J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. USA* **1987**, *84*, 2565–2569.

[11] a) R. C. Scarrow, D. L. White, K. N. Raymond, *J. Am. Chem. Soc.* **1985**, *107*, 6540–6546; b) X. Sun, D. W. Johnson, D. Caulder, K. N. Raymond, E. H. Wong, *J. Am. Chem. Soc.* **2001**, *123*, 2752–2763; c) A. V. Davis, R. M. Yeh, K. N. Raymond, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4793–4796; d) C. Brückner, R. E. Powers, K. N. Raymond, *Angew. Chem.* **1998**, *110*, 1937–1940; *Angew. Chem. Int. Ed.* **1998**, *37*, 1837–1839; e) D. Caulder, C. Brückner, R. E. Powers, S. König, T. N. Parac, J. A. Leary, K. N. Raymond, *J. Am. Chem. Soc.* **2001**, *123*, 8923–8938; f) D. W. Johnson, K. N. Raymond, *Inorg. Chem.* **2001**, *40*, 5157–5161; g) T. N. Parac, D. Caulder, K. N. Raymond, *J. Am. Chem. Soc.* **1998**, *120*, 8003–8004; h) M. Ziegler, J. L. Brumaghim, K. N. Raymond, *Angew. Chem.* **2000**, *112*, 4285–4287; *Angew. Chem. Int. Ed.* **2000**, *39*, 4119–4121.

[12] D. W. Johnson, J. Xu, R. W. Saalfrank, K. N. Raymond, *Angew. Chem.* **1999**, *111*, 3085–3061; *Angew. Chem. Int. Ed.* **1999**, *38*, 2882–2885.

[13] M. Scherer, D. Caulder, D. W. Johnson, K. N. Raymond, *Angew. Chem.* **1999**, *111*, 1690–1694; *Angew. Chem. Int. Ed.* **1999**, *38*, 1588–1592.

[14] a) R. W. Saalfrank, I. Bernt, *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 407–413; b) R. W. Saalfrank, N. Löw, S. Trummer, G. M. Sheldrick, M. Teichert, D. Stalke, *Eur. J. Inorg. Chem.* **1998**, 559–563; c) R. W. Saalfrank, B. Demleitner, in *Transition Metals in Supramolecular Chemistry*; J.-P. Sauvage, Ed.; Wiley, New York, **1999**; Vol. 5; d) R. W. Saalfrank, V. Seitz, F. W. Heinemann, C. Göbel, R. Herbst-Irmer, *J. Chem. Soc. Dalton Trans.* **2001**, 599–603; e) R. W. Saalfrank, H. Maid, N. Mooren, F. Hampel, *Angew. Chem.* **2002**, *114*, 323–326; *Angew. Chem. Int. Ed.* **2002**, *41*, 304–307; f) R. W. Saalfrank, A. Stark, K. Peters, H. G. von Schnering, *Angew. Chem.* **1988**, *100*, 878–880; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 851–853; g) R. W. Saalfrank, H. Glaser, B. Demleitner, F. Hampel, M. M. Chowdhry, V. Schünemann, A. X. Trautwein, G. B. M. Vaughan, R. Yeh, A. V. Davis, K. N. Raymond, *Chem. Eur. J.* **2001**, *7*, 493–497.

[15] R. W. Saalfrank, A. Dresel, V. Seitz, S. Trummer, F. Hampel, M. Teichert, D. Stalke, C. Stadler, J. Daub, V. Schunemann, A. X. Trautwein, *Chem. Eur. J.* **1997**, *3*, 2058–2062.

[16] a) E. C. Constable, S. M. Elder, J. Healy, M. D. Ward, D. A. Tocher, *J. Am. Chem. Soc.* **1990**, *112*, 4590–4592; b) E. C. Constable, A. J. Edwards, P. R. Raithby, D. R. Smith, J. V. Walker, L. Whall, *Chem. Commun.* **1996**, 2551–2552; c) E. C. Constable, D. G. F. Rees, *New J. Chem.* **1997**, *21*, 369–376; d) E. C. Constable, T. Kulke, G. Baum, D. Fenske, *Inorg. Chem. Commun.* **1998**, *1*, 80–82; e) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, *Chem. Eur. J.* **1999**, *5*, 1862–1873; f) C. J. Cathey, E. C. Constable, M. J. Hannon, D. A. Tocher, M. D. Ward, *J. Chem. Soc. Chem. Commun.* **1990**, 621–622.

[17] G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, M. Neuburger, M. Zehnder, *J. Chem. Soc. Dalton Trans.* **2000**, 945–959.

[18] a) P. L. Jones, K. J. Byrom, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Chem. Commun.* **1997**, 1361–1362; b) J. S. Fleming, E. Psillakis, S. M. Couchman, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *J. Chem. Soc. Dalton Trans.* **1998**, 537–543; c) C. R. Rice, C. J. Baylies, L. P. Harding, J. C. Jeffery, R. L. Paul, M. D. Ward, *J. Chem. Soc. Dalton Trans.* **2001**, 3039–3044.

[19] M. Albrecht, *Angew. Chem.* **1999**, *111*, 3671–3674; *Angew. Chem. Int. Ed.* **1999**, *38*, 3463–3465.

[20] C. M. Hartshorn, P. J. Steel, *Chem. Commun.* **1997**, 541–542.

[21] a) J. Fan, J. A. Whiteford, B. Olenyuk, M. D. Levin, P. J. Stang, E. B. Fleischer, *J. Am. Chem. Soc.* **1999**, *121*, 2741–2752; b) B. Olenyuk, J. A. Whiteford, A. Fechtenkötter, P. J. Stang, *Nature* **1999**, *398*, 796–799; c) B. Olenyuk, M. D. Levin, J. A. Whiteford, J. E. Shield, P. J. Stang, *J. Am. Chem. Soc.* **1999**, *121*, 10434–10435; d) F. M. Tabellion, S. R. Seidel, A. M. Arif, P. J. Stang, *Angew. Chem.* **2001**, *113*, 1577–1580; *Angew. Chem. Int. Ed.* **2001**, *40*, 1529–1532; e) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972–983; f) C. J. Kuehl, Y. K. Kryschenko, U. Radhakrishan, S. R. Seidel, S. D. Huang, P. J. Stang, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4932–4936.

[22] a) M. Fujita, *Chem. Soc. Rev.* **1998**, *27*, 417–425; b) D. K. Chand, K. Biradha, M. Fujita, *Chem. Commun.* **2001**, 1652–1653; c) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2001**, 509–518; d) N. Fujita, K. Biradha, M. Fujita, S. Sakamoto, K. Yamaguchi, *Angew. Chem.* **2001**, *113*, 1768–1771; *Angew. Chem. Int. Ed.* **2001**, *40*, 1718–1721; e) M. Yoshizawa, T. Kusukawa, M. Fujita, K. Yamaguchi, *J. Am. Chem. Soc.* **2000**, *122*, 6311–6312; f) M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature* **1995**, *378*, 469–471; g) N. Takeda, K. Umemoto, K. Yamaguchi, M. Fujita, *Nature* **1999**, *398*, 794–796; h) K. Umemoto, H. Tsukui, T. Kusukawa, K. Biradha, M. Fujita, *Angew. Chem.* **2001**, *113*, 2690–2692; *Angew. Chem. Int. Ed.* **2001**, *40*, 2620–2622.

[23] B. F. Abrahams, S. J. Egan, R. Robson, *J. Am. Chem. Soc.* **1999**, *121*, 3535.

[24] a) J. Rebek, Jr., *Chemtracts: Org. Chem.* **1989**, *2*, 59–60; b) E. C. Constable, *Tetrahedron* **1992**, *48*, 10013–10059; c) E. C. Constable, *Nature* **1990**, *346*, 314–315; d) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062; e) E. C. Constable, *Angew. Chem.* **1991**, *103*, 1482–1483; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1450–1451; f) M. Albrecht, *Chem. Soc. Rev.* **1998**, *27*, 281–288; g) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457.

[25] C. Piguet, *J. Inclusion Phenom. Macrocyclic Chem.* **1999**, *34*, 361–391.

[26] a) E. C. Constable, S. M. Elder, J. V. Walker, P. D. Wood, D. A. Tocher, *J. Chem. Soc. Chem. Commun.* **1992**, 229–231; b) R. F. Carina, A. F. Williams, C. Piguet, *Helv. Chim. Acta* **1998**, *81*, 548–557; c) A. F. Williams, C. Piguet, R. F. Carina in *Transition Metals in Supramolecular Chemistry,* (Eds.: L. Fabbrizzi, A. Poggi), Kluwer, Doordrecht, **1994**.

[27] A. F. Williams, R. F. Carina, L. J. Charbonniere, P. G. Desmartin, C. Piguet in *Physical Supramolecular Chemistry* (Eds.: L. Echegoyen, A. E. Kaifer), Kluwer, Doordrecht, **1996**.

[28] M. Meyer, B. Kersting, R. E. Powers, K. N. Raymond, *Inorg. Chem.* **1997**, *36*, 5179–5191.

[29] A. Pfeil, J.-M. Lehn, *J. Chem. Soc. Chem. Commun.* **1992**, 838–840.

[30] a) M. A. Houghton, A. Bilyk, M. M. Harding, P. Turner, T. W. Hambley, *J. Chem. Soc. Dalton Trans.* **1997**, 2725–2733; b) M. Albrecht, O. Blau, *Chem. Commun.* **1997**, 345–346; c) M. Albrecht, O. Blau, R. Fröhlich, *Chem. Eur. J.* **1999**, *5*, 48–56; d) M. Albrecht, *J. Inclusion Phenom. Macrocyclic Chem.* **2000**, *36*, 127–151; e) M. Albrecht, O. Blau, R. Fröhlich, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4876–4872.

[31] M. Albrecht, S. Kotila, *Chem. Commun.* **1996**, 2309–2310.

[32] a) E. C. Constable, F. R. Heirtzler, M. Neuburger, M. Zehnder, *Supramol. Chem.* **1995**, *5*, 197–200; b) E. C. Constable, F. R. Heirtzler, M. Neuburger, M. Zehnder, *Chem. Commun.* **1996**, 933–934; c) E. C. Constable, M. Neuburger, D. R. Smith, M. Zehnder, *Chem. Commun.* **1996**, 1917–1918; d) E. C. Constable, F. R. Heirtzler, M. Neuburger, M. Zehnder, *J. Am. Chem. Soc.* **1997**, *119*, 5606–5617; e) M. Albrecht, R. Fröhlich, *J. Am. Chem. Soc.* **1997**, *119*, 1656–1661; f) M. Albrecht, O. Blau, H. Röttele, *New J. Chem.* **2000**, *24*, 619–622.

[33] M. J. Hannon, S. Bunce, A. I. Clarke, N. W. Alcock, *Angew. Chem.* **1999**, *111*, 1353–1355; *Angew. Chem. Int. Ed.* **1999**, *38*, 1277–1278.

[34] C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, O. Schaad, *J. Am. Chem. Soc.* **1996**, *118*, 6681–6697.

[35] a) R. Krämer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 5394–5398; b) D. Caulder, K. N. Raymond, *Angew. Chem.* **1997**, *109*, 1508–1510; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1440–1442; c) M. A. Masood, E. J. Enemark, T. D. P. Stack, *Angew. Chem.* **1998**, *110*, 973–977; *Angew. Chem. Int. Ed.* **1998**, *37*, 928–932; d) M. Greenwald, D. Wessely, E. Katz, I. Willner, Y. Cohen, *J. Org. Chem.* **2000**, *65*, 1050–1058; e) M. Albrecht, M. Schneider, H. Röttele, *Angew. Chem.* **1999**, *111*, 512–515; *Angew. Chem. Int. Ed.* **1999**, *38*, 557–559; f) W. Schuh, H. Kopacka, K. Wurst, P. Peringer, *Eur. J. Inorg. Chem.* **2002**, 2202–2206.

[36] a) L. Zelikovich, J. Libman, A. Shanzer, *Nature* **1995**, *374*, 790–792; b) P. K.-K. Ho, S.-M. Peng, K.-Y. Wong, C.-M. Che, *J. Chem. Soc. Dalton Trans.* **1996**, 1829–1834; c) M. Greenwald, M. Eassa, E. Katz, I. Willner, Y. Cohen, *J. Electroanal. Chem.* **1997**, *434*, 77–82; d) L. J. Charbonniere, A. F. Williams, C. Piguet, G. Bernardinelli, E. Rivara-Minten, *Chem. Eur. J.* **1998**, *4*, 485–493; e) A. El-ghayouy, A. Harriman, A. De Cian, J. Fischer, R. Ziessel, *J. Am. Chem. Soc.* **1998**, *120*, 9973–9974; f) M. R. Bermejo, M. Fondo, A. M. Gonzales, O. L. Hoyos, A. Sousa, C. A. McAuliffe, W. Hussain, R. Pritchard, V. M. Novotorsev, *J. Chem. Soc. Dalton Trans.* **1999**, 2211–2218.

[37] a) C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner, *J. Am. Chem. Soc.* **1993**, *115*, 8197–8206; b) C. Piguet, E. Rivara-Minten, G. Hopfgartner, J.-C. G. Bünzli, *Helv. Chim. Acta* **1995**, *78*, 1541–1566; c) C. Piguet, G. Bernardinelli, J.-C. G. Bünzli, S. Petoud, G. Hopfgartner, *J. Chem. Soc. Chem. Commun.* **1995**, 2575–2577; d) N. Martin, J.-C. G. Bünzli, V. McKee, C. Piguet, G. Hopfgartner, *Inorg. Chem.* **1998**, *37*, 577–589; e) C. Edder, C. Piguet, J.-C. G. Bünzli, G. Hopfgartner, *J. Chem. Soc. Dalton Trans.* **1997**, 4657–4663; f) M. Elhabiri, R. Scopelliti, J.-C. G. Bünzli, C. Piguet, *J. Am. Chem. Soc.* **1999**, *121*, 10747–10762; g) C. P. Iglesias, M. Elhabiri, M. Hollenstein, J.-C. G. Bünzli, C. Piguet, *J. Chem. Soc. Dalton Trans.* **2000**, 2031–2043; h) C. Piguet, C. Edder, S. Rigault, G. Bernardinelli, J.-C. G. Bünzli, G. Hopfgartner, *J. Chem. Soc. Dalton Trans.* **2000**, 3999–4006; i) G. K. Patra, I. Goldberg, S. K. Chowdhury, B. C. Maiti, A. Sarkar, P. R. Bangal, S. Chakravorti, N. Chattopadhyay, D. A. Tocher, M. G. B. Drew, G. Mostafa, S. Chowdhury, D. Datta, *New J. Chem.* **2001**, *25*, 1371–1373.

[38] S. L. Larson, S. M. Hendrickson, S. Ferrere, D. L. Derr, C. M. Elliott, *J. Am. Chem. Soc.* **1995**, *117*, 5881–5882.

[39] a) A. El-ghayouy, L. Douce, A. Skoulios, R. Ziessel, *Angew. Chem.* **1998**, *110*, 2327–2331; *Angew. Chem. Int. Ed.* **1998**, *37*, 2205–2208; b) R. Ziessel, *Coord. Chem. Rev.* **2001**, *216/217*, 195–223.

[40] A. Lützen, M. Hapke, J. Griep-Raming, D. Haase, W. Saak, *Angew. Chem.* **2002**, *114*, 2190–2194; *Angew. Chem. Int. Ed.* **2002**, *41*, 2086–2089.

[41] a) I. Meistermann, V. Moreno, M. J. Prieto, E. Moldrheim, E. Sletten, S. Khalid, P. M. Rodger, J. C. Peberdy, C. J. Isaac, A. Rodger, M. J. Hannon, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5069–5074; b) M. J. Hannon, V. Moreno, M. J. Prieto, E. Moldrheim, E. Sletten, I. Meistermann, C. J. Isaac, K. J. Sanders, A. Rodger, *Angew. Chem.* **2001**, *113*, 904–908; *Angew. Chem. Int. Ed.* **2001**, *40*, 879–884.

[42] M. Albrecht, S. Kotila, *Angew. Chem.* **1995**, *107*, 2285–2287; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2134–2137.

[43] M. Albrecht, C. Riether, *Chem. Ber.* **1996**, *129*, 829–832.

[44] M. Albrecht, M. Schneider, H. Röttele, *Chem. Ber.* **1997**, *130*, 615–619.

[45] M. Albrecht, *Chem. Eur. J.* **2000**, *6*, 3485–3489.

[46] E. C. Constable, M. Neuburger, L. Whall, M. Zehnder, *New J. Chem.* **1998**, *22*, 219–220.

[47] W. Zarges, J. Hall, J.-M. Lehn, C. Bolm, *Helv. Chim. Acta* **1991**, *74*, 1843–1852.

[48] J. Xu, T. N. Parac, K. N. Raymond, *Angew. Chem.* **1999**, *111*, 3055–3058; *Angew. Chem. Int. Ed.* **1999**, *38*, 2878–2882.

[49] a) A. Bilyk, M. M. Harding, P. Turner, T. W. Hambley, *J. Chem. Soc. Dalton Trans.* **1994**, 2783–2790; b) A. L. Airey, G. F. Swiegers, A. C. Willis, S. B. Wild, *J. Chem. Soc. Chem. Commun.* **1995**, 695–696.
[50] a) A. Bilyk, M. M. Harding, *J. Chem. Soc. Chem. Commun.* **1995**, 1697–1698; b) A. Bilyk, M. M. Harding, P. Turner, T. W. Hambley, *J. Chem. Soc. Dalton Trans.* **1995**, 2549–2553.
[51] a) E. J. Corey, C. L. Cywin, M. C. Noe, *Tetrahedron Lett.* **1994**, *35*, 69–72; b) E. J. Enemark, T. D. P. Stack, *Angew. Chem.* **1995**, *107*, 1082–1084; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 996–998; c) E. J. Enemark, T. D. P. Stack, *Angew. Chem.* **1998**, *110*, 977–981; *Angew. Chem. Int. Ed.* **1998**, *37*, 932–935.
[52] M. Albrecht, M. Schneider, R. Fröhlich, *New J. Chem.* **1998**, *22*, 753–754.
[53] J. H. Brewster, *Top. Curr. Chem.* **1974**, *47*, 29–71.
[54] a) M. Albrecht, *Synthesis* **1996**, 230–237; b) M. Albrecht, *Tetrahedron* **1996**, *52*, 2385–2394.
[55] M. Albrecht, O. Blau, *Synthesis* **1997**, 213–216.
[56] M. Albrecht, S. Kotila, *Angew. Chem.* **1996**, *108*, 1299–1300; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1208–1210.
[57] M. Albrecht, H. Röttele, P. Burger, *Chem. Eur. J.* **1996**, *2*, 1264–1268.
[58] M. J. Hannon, C. L. Painting, A. Jackson, J. Hamblin, W. Errington, *Chem. Commun.* **1997**, 1807–1808.
[59] a) R. Ziessel, A. Harriman, J. Suffert, M. T. Youinou, A. De Cian, J. Fischer, *Angew. Chem.* **1997**, *109*, 2612–2623; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2509–2511; b) M. J. Hannon, C. L. Painting, W. Errington, *Chem. Commun.* **1997**, 307–308; c) R. Ziessel, A. Harriman, A. El-ghayouy, L. Douce, E. Leize, H. Nierengarten, A. Van Dorsselaer, *New J. Chem.* **2000**, *24*, 729–732; d) N. Yoshida, H. Oshio, T. Ito, *Chem. Commun.* **1998**, 63–64; e) L. J. Childs, N. W. Alcock, M. J. Hannon, *Angew. Chem.* **2001**, *113*, 1113–1115; *Angew. Chem. Int. Ed.* **2001**, *40*, 1079–1081; f) N. Yoshida, H. Oshio, T. Ito, *J. Chem. Soc. Perkin Trans. 2* **1999**, 975–983; g) L. J. Childs, N. W. Alcock, M. J. Hannon, *Angew. Chem.* **2002**, *114*, 4418–4421; *Angew. Chem. Int. Ed.* **2002**, *41*, 4244–4247.
[60] M. J. Hannon, C. L. Painting, N. W. Alcock, *Chem. Commun.* **1999**, 2023–2024.
[61] J. Hamblin, A. Jackson, N. W. Alcock, M. J. Hannon, *J. Chem. Soc. Dalton Trans.* **2002**, 1635–1641.
[62] N. Yoshida, K. Ichikawa, *Chem. Commun.* **1997**, 1091–1092.
[63] a) N. Yoshida, H. Oshio, T. Ito, *J. Chem. Soc. Perkin Trans. 2* **2001**, 1674–1678; b) N. Yoshida, K. Ichikawa, M. Shiro, *J. Chem. Soc. Perkin Trans. 2* **2000**, 17–26.
[64] a) M. Albrecht, S. Kamptmann, R. Fröhlich, *Polyhedron* **2003**, *22*, 643–647; b) M. Albrecht, I. Janser, S. Kamptmann, P. Weis, B. Wibbeling, R. Fröhlich, *Dalton Trans.* **2004**, 37–43.
[65] A. Von Zelewsky, Mamula, O. , *J. Chem. Soc. Dalton Trans.* **2000**, 219–231.
[66] J. Sanmartin, M. R. Bermejo, A. M. Garcia-Deibe, O. Piro, E. E. Castellano, *Chem. Commun.* **1999**, 1953–1954.
[67] M. Hong, G. Dong, D. Chun-ying, L. Yu-ting, M. Quing-Jin, *J. Chem. Soc. Dalton Trans.* **2002**, 3422–3424.
[68] B. Kersting, M. Meyer, R. E. Powers, K. N. Raymond, *J. Am. Chem. Soc.* **1996**, *118*, 7221–7222.
[69] M. Albrecht, M. Schneider, *Eur. J. Inorg. Chem.* **2002**, 1301–1306.
[70] M. Albrecht, *Chem. Eur. J.* **1997**, *3*, 1466–1471.
[71] C. Provent, E. Rivara-Minten, S. Hewage, G. Brunner, A. F. Williams, *Chem. Eur. J.* **1999**, *5*, 3487–3494.
[72] M. Albrecht, M. Schneider, *Chem. Commun.* **1998**, 137–138.
[73] T. B. Karpishin, T. D. P. Stack, K. N. Raymond, *J. Am. Chem. Soc.* **1993**, *115*, 182–192.
[74] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der Organischen Chemie,* 5th ed., Thieme, Stuttgart, **1995**.
[75] P. N. W. Baxter, J.-M. Lehn, K. Rissanen, *Chem. Commun.* **1997**, 1323–1324.
[76] a) D. Zurita, P. Baret, J.-L. Pierre, *New J. Chem.* **1994**, *18*, 1143–1146; b) J. J. Lessmann, W. D. Horrocks, *Inorg. Chem.* **2000**, *39*, 3114–3124.
[77] A. F. Williams, C. Piguet, G. Bernardinelli, *Angew. Chem.* **1991**, *103*, 1530–1532; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1490–1492.
[78] G. Bernardinelli, C. Piguet, A. F. Williams, *Angew. Chem.* **1992**, *104*, 1662–1664; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1622–1624.
[79] D. Caulder, K. N. Raymond, *Acc. Chem. Res.* **1999**, *32*, 975–982.
[80] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326.
[81] a) R. H. Blessing, *Acta Crystallogr Sect. A.* **1995**, *51*, 33–37; b) R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421–426.
[82] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473.

Received: October 6, 2003

Published online: April 26, 2004

