

Catechol imine ligands: from helicates to supramolecular tetrahedra†

Markus Albrecht,*^a Ingo Janser^a and Roland Fröhlich^b

Received (in Cambridge, UK) 15th July 2004, Accepted 21st September 2004

First published as an Advance Article on the web 9th December 2004

DOI: 10.1039/b410828k

Di- and tricatechol imines are easily accessible by condensation of appropriate amines with 2,3-dihydroxybenzaldehyde. Dicatechol imines can be used for the alkali metal template-directed self-assembly of dinuclear triple-stranded helicates or meso-helicates with high diastereoselectivity. Tricatechol imines lead in self-assembly processes to metallosupramolecular 4 : 4 tetrahedra with a huge internal cavity, which is able to encapsulate guest species. Hereby the special features of the imine unit can be used to control the outcome of the self-assembly process.

Introduction

In 1995, nearly one decade ago, dicatechol ligands were introduced for the formation of triple-stranded helicates.¹ Hereby the groups of Stack² and Raymond³ focused on catechol amide derivatives, while we thoroughly investigated alkyl⁴ (and later aryl)⁵ bridged dicatechols. The dicatecholate ligands form negatively charged metal complexes, which is in contrast to the well known cationic helicates from nitrogen donor ligands.^{6,7} Therefore the anionic helicates are able to interact with cations. This opened up an interesting host–guest chemistry and lead to the discovery of templating effects.⁸ It was even possible to induce a preferred helical twist at the helicate by interaction with chiral cations.⁹

In the course of our studies of alkyl bridged dinuclear titanium complexes, we found a way how to selectively form triple-stranded helicates or the corresponding achiral

meso-helicates. Hereby the nature of the alkyl spacer controls the preorganisation of the ligand which leads to a highly diastereoselective self-assembly of the helicates. Due to the preferred zigzag conformation of the alkyl chain, an even number of methylene units in the spacer leads to the helicate, while an odd number results in the formation of the corresponding meso-helicate (“side-by-side complex”,⁶ “mesocate”¹⁰).¹¹

Just recently we started to introduce catechol imines as ligands for the self-assembly of triple-stranded helicates and bigger metallosupramolecular aggregates (Fig. 1). Although a disadvantage of the imines is, that they are easily hydrolyzed, we were attracted by the following features of the imine units:

(i) with the imine nitrogen atoms an additional donor is introduced in the spacer, which can interfere with cation binding and therefore might influence the host–guest chemistry,

(ii) the preferred conformation of the imines should be important for the structures of the helicates, and

(iii) the imines are easily accessible by condensation of simple amines with 2,3-dihydroxybenzaldehyde, which allows a broad screening of ligands with different geometries and of different sizes.

Conformational considerations

In principle catechol imines can be compared to the catechol amides (Fig. 2). In both cases the spacer is attached to the catechol through a diatomic nitrogen–carbon linkage. Both

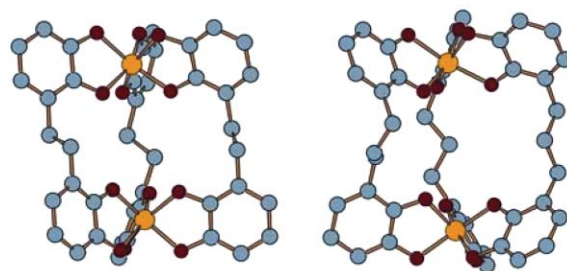


Fig. 1 A dinuclear triple-stranded helicate (left) and a dinuclear triple-stranded meso-helicate (right).

Markus Albrecht was born in 1964 and studied chemistry in Würzburg and Münster. He obtained his Dr. rer. nat. in 1992 with Prof. Dr. G. Erker. After one year as a postdoctoral fellow in the laboratories of Prof. Dr. K. N. Raymond in Berkeley he moved to Karlsruhe and received his habilitation in 1997. Since spring 2002 he has been Professor of Organic Chemistry at the RWTH Aachen. His work was awarded with the “ADUC-Jahrespreis für Habilitanden”, a Heisenberg-fellowship and the “Landeslehrpreis 2002 des Landes Baden-Württemberg”.

Ingo Janser was born in 1970 in Bad Saulgau. He studied chemistry at the University of Karlsruhe and received his Diploma in 2002. In the same year he moved to the RWTH Aachen and is currently finishing his Dr. rer. nat. with a study on helicates and supramolecular containers.

Roland Fröhlich, born in 1952, studied chemistry in Münster and Cologne and received his Dr. rer. nat. in 1982. After postdoctoral studies in the crystallographic institute of the University of Karlsruhe he worked as a sales and applications manager for Enraf Nonius. Since 1993 he has been a senior scientist at the University of Münster and since 1994 a docent for X-ray crystallography at the University of Jyväskylä.

† Dedicated to Professor Jean-Marie Lehn on the occasion of his 65th birthday.

*markus.albrecht@oc.rwth-aachen.de

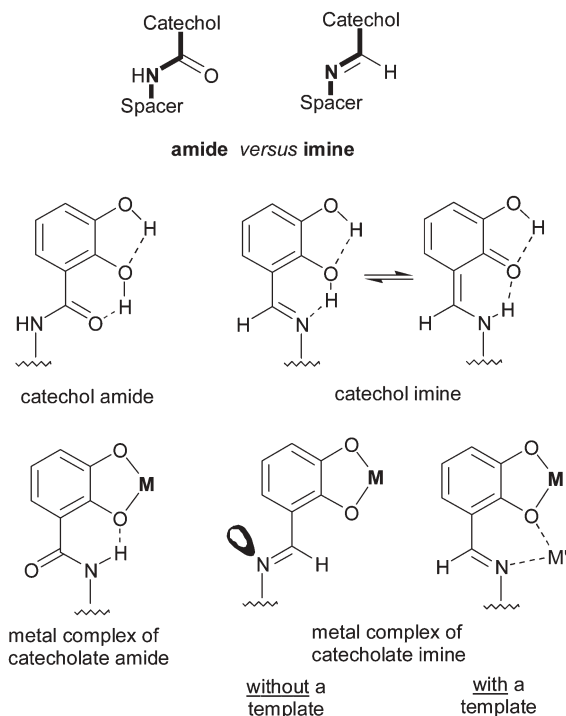


Fig. 2 Comparison of the conformation at a catechol or catecholate amide with the corresponding imines.

atoms of this unit possess sp^2 -hybridization. However, there are some remarkable differences which have to be taken into account.¹²

In the catechol amide two hydrogen bonds are formed. One from the OH group in 3-position of the 2,3-dihydroxybenzoate unit to the oxygen in 2-position and another one between OH in 2-position and the amide oxygen atom. Therefore the amide nitrogen atom, to which a spacer is connected, is orientated opposite to the dihydroxybenzene face.^{13,14}

In the catechol imines the nitrogen atom is orientated towards the hydroxo groups due to strong hydrogen bonding between OH(3) and O(2) and between OH(2) and the imine-N. The latter can be so strong, that proton transfer occurs and a keto-enamine structure is observed.¹⁵

The situation changes upon formation of a chelate complex through the catecholate moiety. In case of the amide, rotation at the aryl-carbonyl bond occurs leading to an NH-O hydrogen bond, which enforces an orientation of the spacer towards the face of the chelating unit.^{13,14} In a metal coordinated imino catecholate, repulsion between the negatively polarized O(2) and the lone pair at nitrogen occurs leading to an outward orientation of the spacer. However, if an appropriate template M' is present, it may be chelated by the internal oxygen of the catecholate and the imine nitrogen and thus will compensate the repulsion and lead to an orientation very similar to the one of the catecholate amide with an N-H-O hydrogen bonded unit.

Differences in the chemistry of catechol amides and catechol imines which result from the different orientations of the catechol-C-N-spacer unit will be shown in this article.

Preparation of di- and tricatechol imine ligands: solid state structures and thermochromic behaviour

Biscatechol imine ligands can be easily prepared by simple imine condensation of appropriate diamines with 2,3-dihydroxybenzaldehyde. Usually the ligands are obtained in pure form by precipitation from an alcoholic solution of the reactants.^{12,16}

The dicatechol ligands which are discussed in this study are shown in Fig. 3. All ligands, except L^5-H_4 were prepared for the first time. L^5-H_4 was already used for the formation of a trinuclear copper(II) complex in which copper is bound to the imine nitrogens and some of the catecholate oxygens while some of the hydroxy groups do not coordinate to the metal.¹⁷ As can be seen from Fig. 3, the size of the ligands was varied from approximately 1 nm (azine linkage in L^1-H_4) to 2 nm length (L^9-H_4).

The use of triamines in the condensation reaction affords the triscatechol derivatives $L^{10}-H_6 - L^{12}-H_6$ (Fig. 4).¹⁶ $L^{12}-H_6$ was already described by Vigato *et al.*¹⁸

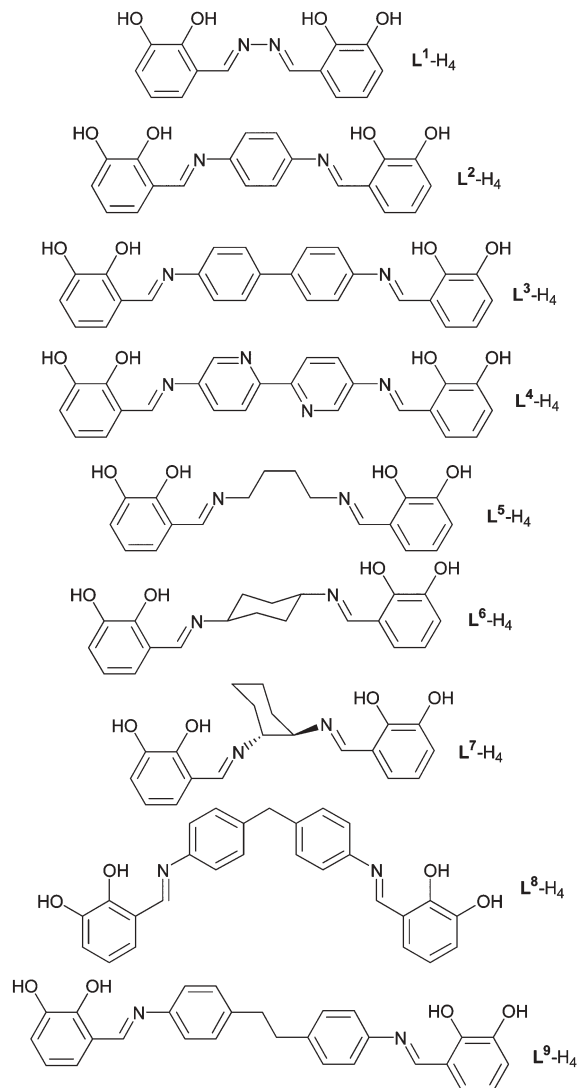


Fig. 3 Biscatechol imine ligands.

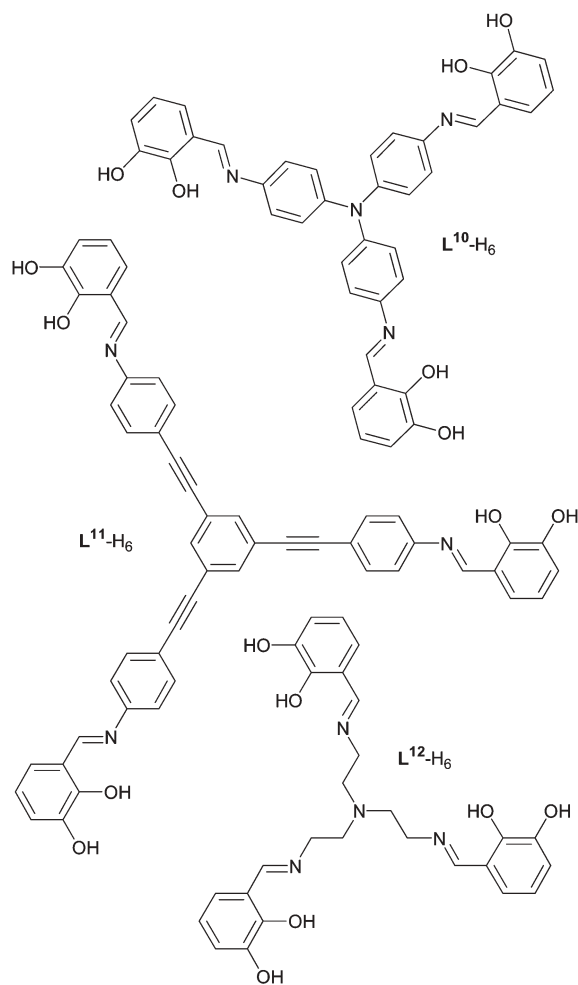


Fig. 4 Triscatechol imine ligands.

The ligands can adopt the catechol imine or the keto-enamine structure as is shown in Figs 2 and 5. The equilibrium between the two different structures is temperature dependent and therefore thermochromic behaviour can be observed for catechol imines.¹⁵ As an example, L^5-H_4 is shown in Fig. 5 at liquid nitrogen temperature (left) and at r.t. (right). The more intense colour at high temperatures is due to the keto-enamine

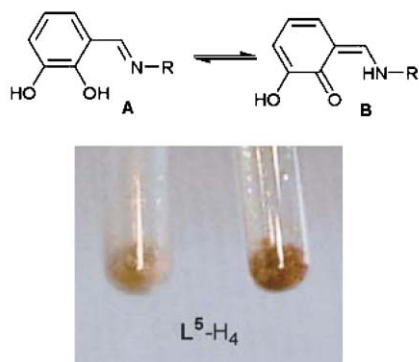


Fig. 5 Thermochromic behavior of L^5-H_4 (left: liquid nitrogen temperature, right: r.t.); adapted from ref. 12.

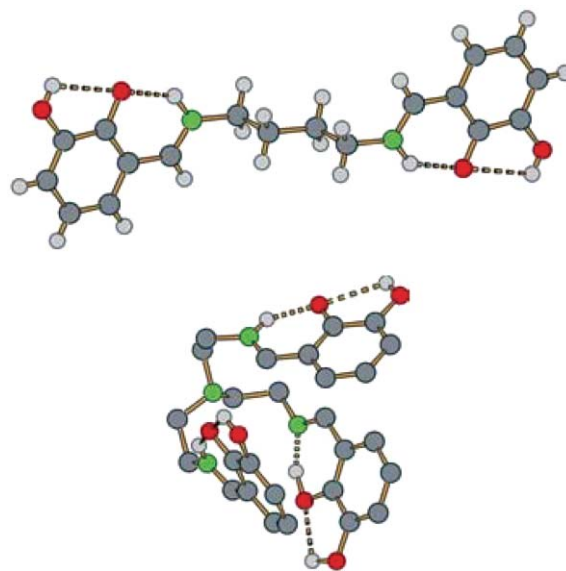


Fig. 6 Solid state structures of L^5-H_4 (top) and $L^{12}-H_6$ (bottom).

structure **B**, while the slightly yellow colour at low temperatures corresponds to the catechol imine **A**.¹² Thermotropic behaviour as observed for our ligands is a well known phenomenon in catechol and salicyl imine chemistry.¹⁵

We obtained X-ray crystal structures of L^5-H_4 and $L^{12}-H_6$ which are depicted in Fig. 6. For L^5-H_4 a hydrogen bonding as shown in Fig. 2 with transfer of the hydrogen from the internal hydroxyl group to the imine nitrogen atom is observed in the solid state. The bond lengths at the catechol imine are in agreement with a keto-enamine structure.¹² In $L^{12}-H_6$ this proton transfer also can be observed, but only at two of the three catechol units. Here we have two keto-enamine and one catechol imine moieties present in the solid state.¹⁶

Dinuclear triple-stranded helicates: self-assembly, templating, diastereoselectivity, and enantiopurity

Disalicyl imines were introduced by Yoshida as ligands for helicates. Hereby the salicylate imines act as bidentate O,N chelating units.¹⁹ Analogously, reaction of ligand L^5-H_4 with copper(II) leads to a bishelical trinuclear complex $[Cu_3(L^5)(L^5-H_2)]$ with two external hydroxyl groups of one strand being uncoordinated but the imine nitrogens binding to the metal.¹⁷

In a first study we investigated the coordination chemistry of the azine bridged ligand L^1-H_4 with titanium(IV) or vanadium(IV) ions in the presence of lithium, sodium or potassium carbonate in methanol. With titanium(IV) orange solids are obtained in quantitative yield, while with vanadium(IV) black solids were formed. In case of the diamagnetic titanium(IV) complexes, NMR spectra can be taken, which show the high symmetry of the complexes. Similar shifts in the 1H NMR spectra of the salts of $M_4[(L^1)_3Ti_2]$ ($M = Li, Na, K$) show that no significant interaction occurs between the helicate and the counteranions. On the other hand, slight differences in the ^{13}C NMR shift of the imine carbon resonance indicate weak interactions between the anion and alkali metal cations in solution.²⁰

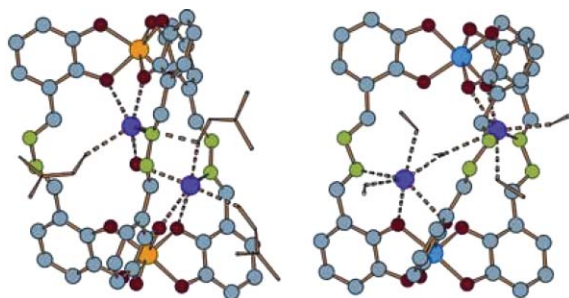


Fig. 7 Parts of the X-ray structures of $\text{Na}_4[(\text{L}^1)_3\text{Ti}_2]$ (from DMF, left) and $\text{Na}_4[(\text{L}^1)_3\text{V}_2]$ (from methanol, right). Colour code (through the whole manuscript): grey: C, red: O, green: N, dark blue: Na, orange: titanium, light blue: vanadium; solvent molecules are only indicated.

Fig. 7 shows parts of the X-ray structures of $\text{Na}_4[(\text{L}^1)_3\text{Ti}_2]$ (from DMF) and $\text{Na}_4[(\text{L}^1)_3\text{V}_2]$ (from methanol). The tetra-anionic dinuclear complexes $[(\text{L}^1)_3(\text{Ti/V})_2]^{4-}$ adopt the structure of a triple-stranded helicate with metal-metal separations of 8.699 Å (Ti–Ti) and 8.339 Å (V–V). In each case, two of the sodium counterions are bound in the interior of the helicate, coordinating to internal catecholate oxygen atoms, some of the imine nitrogens, and are coordinatively saturated by solvent molecules or water. The cavity of the helicate is too small to encapsulate two cations fully and therefore they are forced to bind in an unsymmetrical fashion, enforcing an involvement of the imines into cation binding in the solid state.^{20,21}

As can be seen from the two X-ray structures, the length of the cylinder-type helicates $[(\text{L}^1)_3\text{Ti/V}_2]^{4-}$ is close to 10 Å. This size can be easily extended by formally inserting long rigid units into the N–N bond of the azine. Thus, titanium complexes with 1,4-phenylene ($\text{L}^2\text{-H}_4$) and 4,4'-biphenylene ($\text{L}^3\text{-H}_4$) as spacers were prepared. Due to the low solubility, the coordination studies with titanium(IV) ions have to be performed in DMF as solvent. The structures of the triple-stranded helicates $[(\text{L}^2)_3\text{Ti}_2]^{4-}$ and $[(\text{L}^3)_3\text{Ti}_2]^{4-}$ are depicted in Fig. 8. Introduction of phenylene as a spacer leads to an Ti–Ti

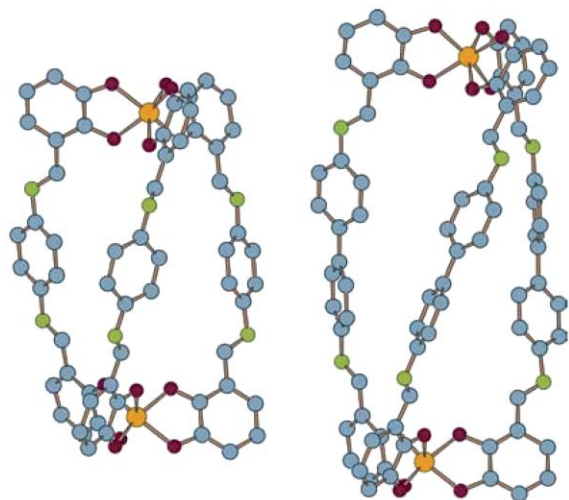


Fig. 8 Parts of the X-ray structures of $\text{K}_4[(\text{L}^2)_3\text{Ti}_2]$ and $\text{Na}_4[(\text{L}^3)_3\text{Ti}_2]$.

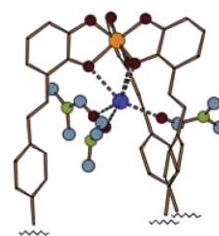


Fig. 9 Coordination at encapsulated sodium (blue) in $\text{Na}_4[(\text{L}^3)_3\text{Ti}_2]$.

separation of approximately 12.6 Å in $[(\text{L}^2)_3\text{Ti}_2]^{4-}$, while the biphenyl spacer of $[(\text{L}^3)_3\text{Ti}_2]^{4-}$ results in a Ti–Ti distance of 16.9 Å. In the latter case, the length of the whole cylindrical complex is about 21 Å. Due to the rigidity and linearity of the spacer, the complexes possess the homochiral helicate structures with the ligands slightly wrapping around the Ti–Ti axis and thus transferring the stereochemical information from one complex unit to the other.^{12,21}

In contrast to the azine bridged complexes $\text{M}_4[(\text{L}^1)_3(\text{Ti/V})_2]$ those with the ligands L^2 and L^3 have enough internal space available to fully encapsulate two counterions. In $\text{K}_4[(\text{L}^2)_3\text{Ti}_2]$ two potassium ions each are binding to three internal catecholate oxygens and to three DMF molecules. Thus a K–K distance of approximately 5.5 Å results, which is ideal for the coordination of an additional bridging water molecule inside of the helicate.¹² The typical coordination environment of an encapsulated sodium cation in $\text{Na}_4[(\text{L}^3)_3\text{Ti}_2]$ is shown in Fig. 9. The cations are separated by 10.6 Å, leaving enough space for the inclusion of an additional DMF molecule in between them.²¹

The bipyridine bridged ligand $\text{L}^4\text{-H}_4$ leads to results which are similar to those with the biphenyl spacer. An X-ray structural analysis shows the structural similarity between the helicates $\text{Na}_4[(\text{L}^3)_3\text{Ti}_2]$ and $\text{Na}_4[(\text{L}^4)_3\text{Ti}_2]$.²²

A strong templating effect by the alkali metal cations was observed in our earlier investigations on alkyl bridged triple-stranded helicates.⁸ With the rigid catechol imine ligands L^1 , L^2 and L^3 helicates are obtained which encapsulate cations in their interior, but no influence of those cations on the formation of the dinuclear complexes can be shown.

However, with alkyl bridged dicatechol imines $\text{L}^5\text{-H}_4$, $\text{L}^6\text{-H}_4$ and $\text{L}^7\text{-H}_4$ an influence of the counterions can be observed. The self-assembly of triple-stranded dinuclear complexes proceeds smoothly if sodium or potassium cations are present. NMR spectroscopy shows nicely resolved spectra which indicate the high symmetry of the coordination compounds. With lithium no defined compounds but rather mixtures of oligomers are obtained.¹²

Fig. 10 presents the X-ray structures of the triple-stranded helicates $[(\text{L}^6)_3\text{Ti}_2]^{4-}$ and $[(\text{L}^7)_3\text{Ti}_2]^{4-}$. Again two of the counterions are found in each of the cavities.¹²

In $[(\text{L}^6)_3\text{Ti}_2]^{4-}$ the *trans*-1,4-substituted cyclohexane can adopt a favorable conformation with the substituents in equatorial position. A Ti–Ti separation of 12.475 Å results. $[(\text{L}^7)_3\text{Ti}_2]^{4-}$, on the other hand, has to adopt a diaxial conformation at the *trans*-(*R,R*)-cyclohexane and the Ti–Ti distance is only 10.264 Å due to the shorter carbon chain length (C_2 in L^7 versus C_4 in L^6).¹²

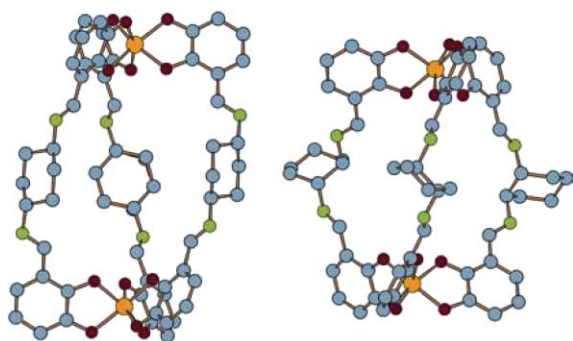


Fig. 10 Parts of the X-ray structures of $\text{Na}_4[(\text{L}^6)_3\text{Ti}_2]$ and $\text{K}_4[(\text{L}^7)_3\text{Ti}_2]$.

Usually the helicates are formed as racemic mixtures of the Λ, Λ - and Δ, Δ -stereoisomer. However, ligand L^7 bears chiral information hidden in the spacer. This is transferred to the metal centers and an enantiomerically pure triple-stranded helicate is formed which possesses a left handed helical twist. In $\text{K}_4[(\text{L}^7)_3\text{Ti}_2]$ the 1,2-(*R,R*)-cyclohexyl spacer induces Λ -configuration at each of the two titanium(IV) triscatecholate units.²³

The ligands L^1 – L^7 all lead to chiral helicates. However, in case of alkyl-bridged dicatechols the achiral meso-helicates could be obtained as well. We wanted to know, if we are also able to control the diastereoselectivity of helicate *versus* meso-helicate formation in case of catechol imine ligands. We even challenged ourselves, to control the transfer of stereochemical information over a long distance by only small stereocontrolling units. The general concept is shown in Fig. 11.

The stereochemical information of one metal complex unit should be transferred through a rigid linear connector (composed of the imine unit and a phenylene moiety) to a central stereocontrolling unit, which “processes” this information and transfers it—again through a linear connector—to the second metal complex. The stereocontrolling unit can be

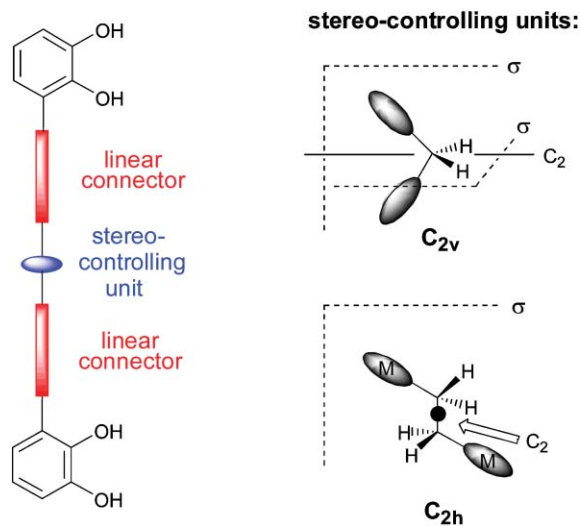


Fig. 11 Concept for the stereo control of helicate *versus* meso-helicate formation with long dicatechol imine ligands possessing rigid linear connecting units and small (CH_2 or CH_2CH_2) stereo controlling units.

either an ethylene group, which in its preferred zigzag conformation possesses a C_2 axis which is relevant for the formation of the dinuclear helicate. A methylene unit as stereocontrolling unit possesses two symmetry elements which have to be considered. The C_2 axis could favour the formation of the helicate, while a “dominance” of the σ -plane would support the preferred formation of the meso-helicate.²¹

The derivatives L^8 - H_4 and L^9 - H_4 were used to test this concept on the long-range stereocontrol in dinuclear helicate-type complexes. Coordination studies of the ligands with titanium(IV) ions in the presence of M_2CO_3 ($\text{M} = \text{Li}, \text{Na}, \text{K}$) affords the dinuclear complexes $\text{M}_4[(\text{L}^8)_3\text{Ti}_2]$ and $\text{M}_4[(\text{L}^9)_3\text{Ti}_2]$, which both show high symmetry by NMR spectroscopy.

X-ray structural analyses of the sodium salts reveal, that $\text{M}_4[(\text{L}^8)_3\text{Ti}_2]$ adopts the achiral meso-helicate structure, while $\text{M}_4[(\text{L}^9)_3\text{Ti}_2]$ represents the chiral helicate (Fig. 12).

The result obtained for the homochiral helicate $\text{Na}_4[(\text{L}^9)_3\text{Ti}_2]$ is expected from the symmetry of the central ethylene unit (see Fig. 11). However, the observation of only the meso-helicate in case of $\text{Na}_4[(\text{L}^8)_3\text{Ti}_2]$ is rather surprising. For symmetry reasons both diastereomers (homochiral or heterochiral) could be formed. Furthermore, NMR spectroscopic investigations at variable temperature reveal, that for $\text{M}_4[(\text{L}^8)_3\text{Ti}_2]$ the meso-helicate is the only species which can be observed in solution.

The preferred formation of the meso-helicate with ligand L^8 is tentatively attributed to a higher degree of flexibility of the dinuclear complex compared to the corresponding homochiral

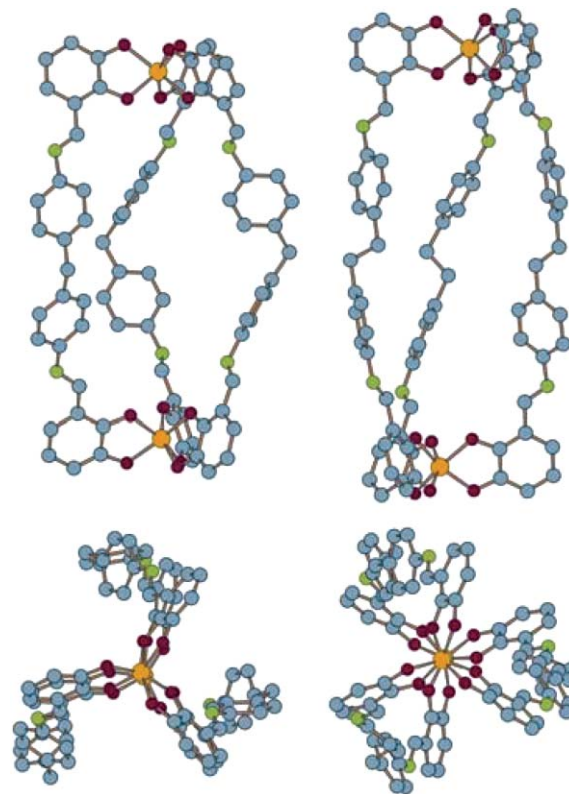


Fig. 12 Parts of the X-ray structures of the meso-helicate $[(\text{L}^8)_3\text{Ti}_2]^{4-}$ (left) and the helicate $[(\text{L}^9)_3\text{Ti}_2]^{4-}$ (right); top: side view, bottom: top view along the Ti–Ti axis.

helicate. Therefore in $[(L^8)_3Ti_2]^{4-}$ the heterochiral form should be favoured due to entropic reasons.²¹

Nevertheless, in $[(L^8)_3Ti_2]^{4-}$ and $[(L^9)_3Ti_2]^{4-}$ the stereochemical information of one titanium triscatecholate unit is transferred over approximately 1 nm to a small alkyl group which controls the stereochemistry at a second complex unit which again is located 1 nm away.

The helicates $[(L^8)_3Ti_2]^{4-}$ and $[(L^9)_3Ti_2]^{4-}$ form cylinders with a length of more than 2 nm. They have an internal cavity, which is big enough to encapsulate two $\{Na(DMF)_3\}$ units and one central DMF molecule.²¹

The described results show, that biscatechol imines are well suited to form dinuclear triple-stranded helicates or meso-helicates with high diastereoselectivity in self-assembly processes. Encapsulation of alkali metal cations in the interior of the coordination compounds seems to be important for their formation. However, it would be of general interest, to obtain related self-assembled metallosupramolecular aggregates with a larger internal cavity to investigate host-guest chemistry or even perform chemical reactions inside. Therefore we switched from dicatechol to tricatechol imine ligand systems.

Supramolecular tetrahedra

Ligands with three bidentate metal binding sites which possess an axis of C_3 -symmetry in their idealized structure are able to form tetrahedral 4 : 4 complexes with metal ions that prefer an octahedral coordination geometry.²⁴ Many examples are described in the literature, where tetrahedral 6 : 4 complexes are obtained.²⁵ Some of Fujita's coordination compounds can be considered as supramolecular tetrahedra,²⁶ as well as the example by Müller and Robson.²⁷ However, the ligands depicted in Fig. 13 were shown to form 4 : 4 tetrahedral

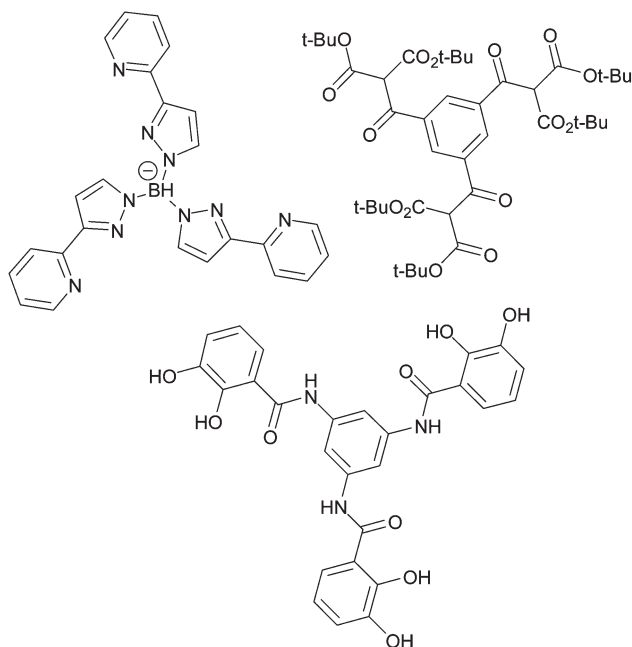


Fig. 13 Ligands for 4 : 4 supramolecular tetrahedral coordination compounds.

coordination compounds. Unfortunately the size of the tetrahedra is too small to bind guest species in the interior.^{14,28}

Our aim is to obtain larger tetrahedral complexes which are able to bind molecules in their interior.^{26,29} The triscatechol imine ligands L^{10} -H₆ and L^{11} -H₆ were introduced by us for this purpose.

Complexation of L^{10} -H₆ or L^{11} -H₆ with titanium(IV) ions in the presence of alkali metal carbonate as base ($M = Li, Na, K$) in DMF produces in clean self-assembly processes coordination compounds $M_8[(L^{10})_4Ti_4]$ and $M_8[(L^{11})_4Ti_4]$. NMR spectroscopy reveals the high symmetry of the coordination compounds while ESI MS shows that the desired 4 : 4 complexes are formed.³⁰

We were able to obtain crystals of $K_8[(L^{10})_4Ti_4]$ which could be solved by X-ray structural analysis showing the structure to be a supramolecular tetrahedron with the titanium(IV) ions sitting at the corners and the " C_3 "-symmetric ligands located at the faces.

Fig. 14 shows the tetrahedron with the titanium(IV) ions separated by approximately 16 Å. The length of the edge of the

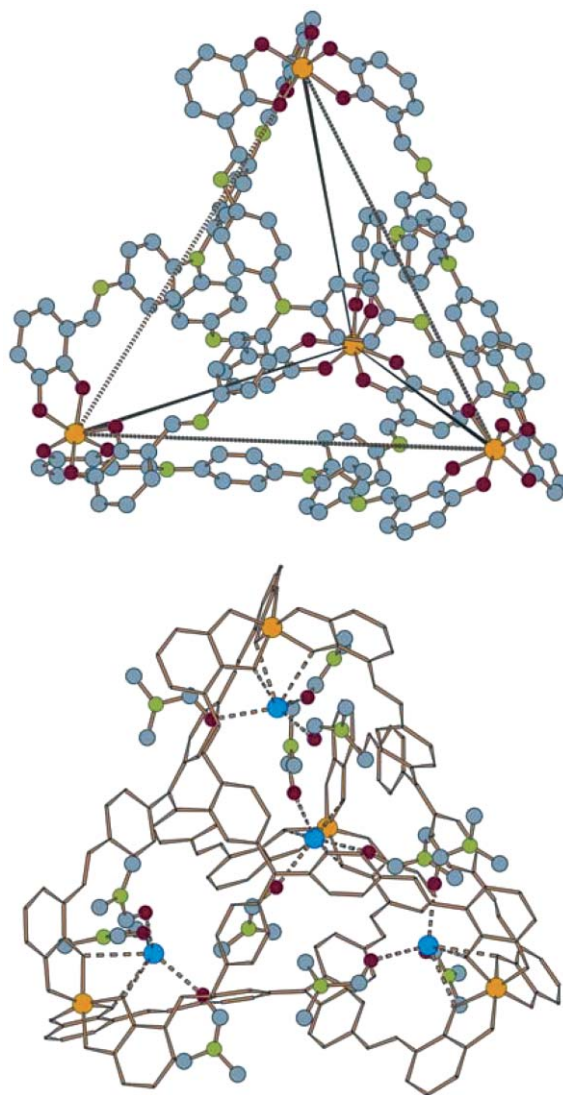


Fig. 14 The molecular tetrahedron $[(L^{10})_4Ti_4]^{8-}$ in the solid state (top) and the four encapsulated $\{K(DMF)_3\}$ -units (bottom).

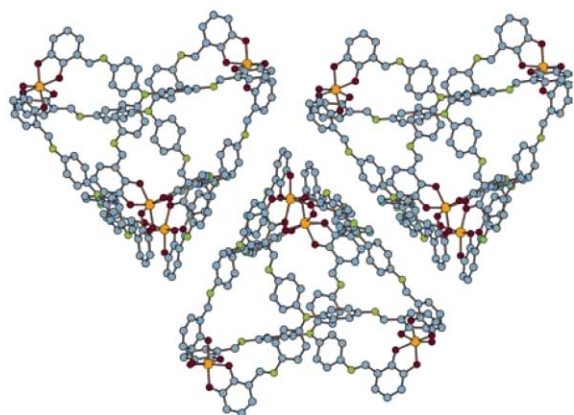


Fig. 15 Stacking of the tetrahedra $[(L^{10})_4Ti_4]^{8-}$ in the solid phase.

tetrahedron is about 2.0 nm. (In the case of $M_8[(L^{11})_4Ti_4]$ this length should be more than 2.5 nm). The octaanionic complex $[(L^{10})_4Ti_4]^{8-}$ possesses a huge internal cavity with four potassium cations bound to the internal catecholate oxygen atoms of each titanium(IV) catecholate complex unit. Additionally three DMF molecules are binding to each of the potassium ions.

In the solid state the tetrahedra stack face to face and the crystal structure, which is depicted in Fig. 15, is formed.³⁰

$L^{10}-H_6$ and $L^{11}-H_6$ are both rigid ligand systems which are forced by their geometry to form the supramolecular tetrahedra. However, we were interested, if it is also possible to obtain such 4 : 4 complexes with the flexible ligand $L^{12}-H_6$. Hereby the preferred conformation of the imino catecholate unit should be in favour for the formation of the tetrahedron. Therefore we used $L^{12}-H_6$ for complexation of titanium(IV) ions. $L^{12}-H_6$ was already used by Vigato *et al.* as an N_3O_3 ligand.¹⁸

Several years ago, Raymond and coworkers investigated the coordination behaviour of the triscatechol amide ligand TRENcam and showed that it is a very good chelating ligand for different metal ions. Binding of the metal hereby is supported by strong intramolecular amide-NH catecholate-O hydrogen bonding.³¹ However, if the triscatechol imine ligand $L^{12}-H_6$ is deprotonated, the catecholates orientate “outwards” due to the repulsion of the oxygen and nitrogen lone pairs. This should favour the formation of a 4 : 4 over a 1 : 1 complex (Fig. 16).

Reaction of $L^{12}-H_6$ with titanium(IV) ions and potassium carbonate in DMF leads to a mixture of oligomeric complexes. However, if the reaction is performed with sodium carbonate or if sodium salts are added to the mixture, a well defined coordination compound is obtained.³²

An X-ray structural analysis shows that the mononuclear complex $Na[Na \subset \{(L^{12})Ti\}]$ is formed, in which sodium acts as a template and stabilizes the mononuclear titanium(IV) complex. Na^+ coordinates to the internal catecholate oxygens and the nitrogen atoms of L^{12} and thus compensates the repulsion of the ligand lone pairs (Fig. 17).

Potassium is bigger than sodium and therefore it cannot act in a similar fashion. However, crystallization of the mixture of oligomers, which are formed from L^{12} and titanium(IV) in the

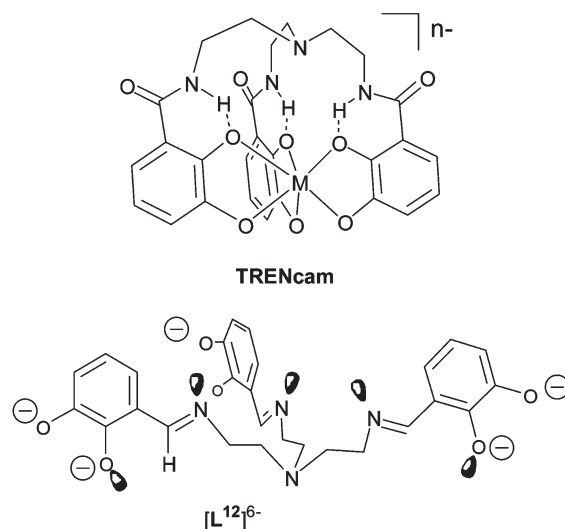


Fig. 16 Comparison of TRENcam and ligand L^{12} .

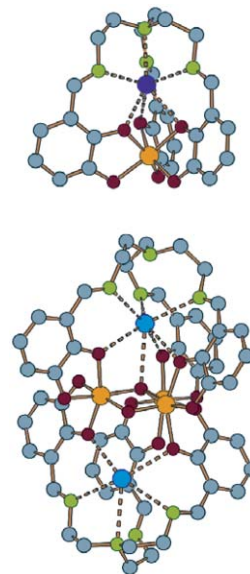


Fig. 17 Structure of $[Na \subset \{(L^{12})Ti\}]^-$ (top) and $[K_2 \subset \{(L^{12})_2(Ti_3O_2)\}]^{2-}$ (bottom).

presence of potassium carbonate results in a few crystals of $K_2[K_2 \subset \{(L^{12})_2(Ti_3O_2)\}]$. Potassium cations bind to the nitrogen atoms of the ligand. This stretches the size of the triscatechol ligand and not only one titanium(IV) but a Ti_3O_2 cluster can be coordinated to the ligand. One of the ligands is approaching from the top, the other from the bottom forming two cavities for the binding of two potassium cations. Here the size of the titanium complexes adjusts to the size of the templating potassium ions.

In the coordination compounds $[Na \subset \{(L^{12})Ti\}]^-$ and $[K_2 \subset \{(L^{12})_2(Ti_3O_2)\}]^{2-}$ the alkali metal cations compensate the repulsion of the ligand lone pairs. However, to use the repulsion for the formation of the tetrahedron, we have to suppress the cation binding. Therefore we dissolved the oligomeric mixture of coordination compounds of ligand L^{12}

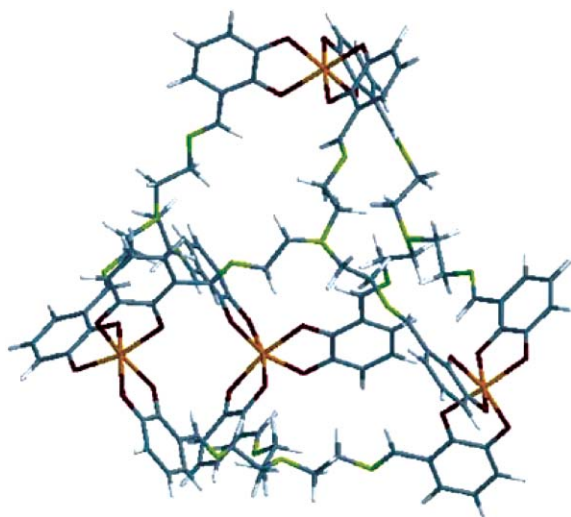


Fig. 18 Proposed structure of $[(L^{12})_4Ti_4]^{8-}$ as generated by MMFF calculations (Spartan O2).

in DMSO- d_6 , which should be a slightly better ligand for potassium than DMF is.

Within a few hours the spectrum changes and a dominating single set of signals of a highly symmetric species can be observed. The observation of the resonance of the imine protons at $\delta = 8.6$ indicates its “inward” orientation towards the catecholate oxygen. This is in favour for a multinuclear coordination compound. Finally, ESI MS shows, that here the supramolecular tetrahedron $[(L^{12})_4Ti_4]^{8-}$ is present (Fig. 18). The corresponding peaks are observed at $m/z = 795.6$ $\{K_5[(L^{12})_4Ti_4]\}^{3-}$, 783.3 $\{HK_4[(L^{12})_4Ti_4]\}^{3-}$, 770.6 $\{H_2K_3[(L^{12})_4Ti_4]\}^{3-}$, 587.7 $\{K_4[(L^{12})_4Ti_4]\}^{4-}$, and 577.8 $\{HK_3[(L^{12})_4Ti_4]\}^{4-}$.³²

The investigations with ligand L^{12} show, how crucial templating effects of cations can be in the self-assembly processes of metallosupramolecular aggregates. If we are able to control this templating, we can direct our self-assembly towards the formation of different well-defined coordination compounds.

Conclusions

Dinuclear triple-stranded helicates and meso-helicates as well as tetranuclear 4 : 4 tetrahedral coordination compounds were described in this article. All the compounds contain as a special feature the catecholate imine unit as metal coordination site. This unit shows versatile coordination behaviour due to its preferred conformation and the influence of alkali metal cations on this conformation. Templating plays an important role in the formation of well-defined supramolecular aggregates from catechol imines. This is in strong contrast to the well known conformationally fixed catechol amides.

In the course of our investigations we observed interesting temperature dependent proton transfer behaviour, we were able to obtain helicates in enantiomeric pure form by introduction of chiral spacers and we succeeded to control the relative stereochemistry of dinuclear complexes over a distance of nearly 2 nm.

The formation of huge supramolecular tetrahedra is just the starting point for some host–guest chemistry in the interior of the aggregate as it is successfully described by Raymond³³ or Fujita.³⁴

The ease to prepare oligocatechol imines opens up a wide field of research which can be systematically studied or might be screened by combinatorial methods.

However, we are still excited to go on with our research to develop new systems and in the future will direct our studies towards the application of the self-assembled aggregates in catalysis or material science.³⁵

This work was supported by the priority program “Sekundäre Wechselwirkungen als Steuerungsprinzipien zur gerichteten Funktionalisierung reaktionsträger Substrate” of the Deutsche Forschungsgemeinschaft. Support by the SFB 380 is also gratefully acknowledged. We thank Dr. Patrick Weis (Karlsruhe) for taking numerous FT-ICR-ESI MS spectra.

Markus Albrecht,^{*a} Ingo Janser^a and Roland Fröhlich^b

^aInstitut für Organische Chemie der RWTH-Aachen,

Professor-Pirlet-Str. 1, 52074 Aachen, Germany.

E-mail: markus.albrecht@oc.rwth-aachen.de

^bOrganisch-Chemisches Institut, Universität Münster, Corrensstr. 40, 48149 Münster, Germany

Notes and references

- For examples of the pioneering work on double- and triple-stranded helicates by J.-M. Lehn, see: J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier and D. Moras, *Proc. Natl. Acad. Sci. U.S.A.*, 1987, **84**, 2565; R. Krämer, J.-M. Lehn, A. DeCian and J. Fischer, *Angew. Chem.*, 1993, **105**, 764, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 703.
- E. J. Enemark and T. D. P. Stack, *Angew. Chem.*, 1995, **107**, 1082, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 996; E. J. Enemark and T. D. P. Stack, *Inorg. Chem.*, 1996, **35**, 2719.
- B. Kersting, M. Meyer, R. E. Powers and K. N. Raymond, *J. Am. Chem. Soc.*, 1996, **118**, 7221; D. Caulder and K. N. Raymond, *Angew. Chem.*, 1997, **109**, 1508, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1440; M. Meyer, B. Kersting, R. E. Powers and K. N. Raymond, *Inorg. Chem.*, 1997, **36**, 5179.
- M. Albrecht and S. Kotila, *Angew. Chem.*, 1995, **107**, 2285, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2134; M. Albrecht and S. Kotila, *Angew. Chem.*, 1996, **108**, 1299, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1208.
- M. Albrecht, M. Schneider and R. Fröhlich, *New J. Chem.*, 1998, 753; M. Albrecht and M. Schneider, *Eur. J. Inorg. Chem.*, 2002, 1301.
- C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005.
- M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457; M. J. Hannon and L. J. Childs, *Supramol. Chem.*, 2004, **16**, 7.
- M. Albrecht, *Chem. Soc. Rev.*, 1998, **27**, 281.
- R. M. Yeh, M. Ziegler, D. W. Johnson, A. J. Terpin and K. N. Raymond, *Inorg. Chem.*, 2001, **40**, 2216.
- J. Xu, T. N. Parac and K. N. Raymond, *Angew. Chem.*, 1999, **111**, 3055, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 2878.
- M. Albrecht, *Chem. Eur. J.*, 2000, **6**, 3485.
- M. Albrecht, I. Janser, S. Kamptmann, P. Weis, B. Wibbeling and R. Fröhlich, *Dalton Trans.*, 2004, 37.
- T. B. Karpishin, T. D. P. Stack and K. N. Raymond, *J. Am. Chem. Soc.*, 1993, **115**, 6115.
- D. Caulder, C. Brückner, R. E. Powers, S. König, T. N. Parac, J. A. Leary and K. N. Raymond, *J. Am. Chem. Soc.*, 2001, **123**, 8923.
- H. Pizzala, M. Carles, W. E. E. Stone and A. Thevand, *J. Chem. Soc., Perkin Trans. 2*, 2000, 935.
- M. Albrecht, I. Janser and R. Fröhlich, *Synthesis*, 2004, 1977.

-
- 17 J. Sanmartin, M. R. Bermejo, A. M. Garcia-Deibe, O. Piro and E. E. Castellano, *Chem. Commun.*, 1999, 1953.
- 18 A. Aguiari, E. Bullita, U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato and U. Russo, *Inorg. Chim. Acta*, 1994, **219**, 135; A. Aguiari, E. Bullita, U. Casellato, P. Guerriero, S. Tamburini and P. A. Vigato, *Inorg. Chim. Acta*, 1992, **202**, 157.
- 19 N. Yoshida, H. Oshio and T. Ito, *Chem. Commun.*, 1998, 63.
- 20 M. Albrecht, S. Kamptmann and R. Fröhlich, *Polyhedron*, 2003, **22**, 643.
- 21 M. Albrecht, I. Janser, H. Houjou and R. Fröhlich, *Chem. Eur. J.*, 2004, **10**, 2839.
- 22 M. Albrecht, I. Janser, M. Hapke, P. Weis and R. Fröhlich, *Chem. Eur. J.*, submitted for publication.
- 23 M. Albrecht, I. Janser, J. Fleischhauer, Y. Wang, G. Raabe and R. Fröhlich, *Mendeleev Commun.*, in press.
- 24 M. Albrecht, *Angew. Chem.*, 1999, **111**, 3671, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 3463; D. Caulder and K. N. Raymond, *J. Chem. Soc., Dalton Trans.*, 1999, 1185; S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853.
- 25 R. W. Saalfrank and B. Demleitner, in 'Ligand and Metal control of self-assembly in supramolecular chemistry', ed. J.-P. Sauvage, New York, 1999; R. W. Saalfrank, A. Stark, K. Peters and H. G. Von Schnering, *Angew. Chem.*, 1988, **100**, 878, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 851.
- 26 M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa and K. Biradha, *Chem. Commun.*, 2001, 509.
- 27 B. F. Abrahams, S. J. Egan and R. Robson, *J. Am. Chem. Soc.*, 1999, **121**, 3535.
- 28 A. J. Amoroso, J. C. Jefferey, P. L. Jones, J. A. McCleverty, P. Thornton and M. D. Ward, *Angew. Chem.*, 1995, **107**, 1577, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1443; C. Brückner, R. E. Powers and K. N. Raymond, *Angew. Chem.*, 1998, **110**, 1937, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1837; 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 and K. N. Raymond, *Chem. Eur. J.*, 2002, **8**, 493; R. L. Paul, A. J. Amoroso, P. L. Jones, S. M. Couchman, Z. R. Reeves, L. H. Rees, J. C. Jefferey, J. A. McCleverty and M. D. Ward, *Dalton Trans.*, 1999, 1563.
- 29 M. Yoshizawa, T. Kusukawa, M. Fujita and K. Yamaguchi, *J. Am. Chem. Soc.*, 2000, **122**, 6311.
- 30 M. Albrecht, I. Janser, S. Meyer, P. Weis and R. Fröhlich, *Chem. Commun.*, 2003, 2854.
- 31 S. J. Rodgers, C. W. Lee, C. Y. Ng and K. N. Raymond, *Inorg. Chem.*, 1987, **26**, 1622; T. M. Garrett, P. W. Miller and K. N. Raymond, *Inorg. Chem.*, 1989, **28**, 128.
- 32 M. Albrecht, I. Janser, J. Runsink, G. Raabe, P. Weis and R. Fröhlich, *Angew. Chem.*, in press.
- 33 D. H. Leung, D. Fiedler, R. G. Bergman and K. N. Raymond, *Angew. Chem.*, 2004, **116**, 981, *Angew. Chem., Int. Ed. Engl.*, 2004, **43**, 963.
- 34 M. Yoshizawa, Y. Takeyama, T. Okano and M. Fujita, *J. Am. Chem. Soc.*, 2003, **125**, 3243.
- 35 C. A. Schalley, A. Lützen and M. Albrecht, *Chem. Eur. J.*, 2004, **10**, 1072.