Benzene-*o*-dithiolate ligands as versatile building blocks in supramolecular chemistry

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Polydentate ligands with benzene-*o*-dithiolato donor groups are useful building blocks in supramolecular coordination chemistry. The coordination chemistry of bis- and tris(benzene-*o*-dithiolato) ligands and mixed benzene-*o*-dithiolato/catecholato ligands is reviewed. These ligands exhibit a versatile coordination chemistry both in solution and in the solid state.

1 Introduction

Octahedral (*OC*) coordination is by far the most common coordination geometry encountered in six-coordinate complexes, mainly due to the minimization of steric interactions between the ligands and often leading to a maximization of the ligand field stabilization energy. The trigonal-prismatic (*TPY*) coordination geometry, on the other hand, was for a long time only known in the solid state for compounds such as MoS_2,[1] WS_2[2] and $NiAs$[3] and this unusual geometry was attributed to packing effects in the crystal lattice. The discovery of the first trigonal-prismatic molecular compounds $[Re(S_2C_2Ph_2)_3]$,[4] $[Mo(S_2C_2H_2)_3]$[5] and $[V(S_2C_2Ph_2)_3]$[6] led to an intensive search for trigonal-prismatic complexes and an ongoing discussion about the reasons responsible for the preference of the *TPY* over the *OC* coordination geometry. Although the *TPY*

coordination geometry has been established for a few permethylated complexes such as $[W(CH_3)_6]$,[7,8] $[Re(CH_3)_6]$,[7,8] $[Mo(CH_3)_6]$,[9] $[Li(tmed)]_2[Zr(CH_3)_6]$[10] and $[Li(OEt_2)_3]$ $[Ta(CH_3)_6]$,[8] in addition to some complexes with macrobicyclic tris(catechoylamide) ligands,[11] mainly complexes of unsaturated dithiolato ligands such as A^{2-}–E^{2-} have been shown to form trigonal-prismatic coordination compounds (Fig. 1).

Among the *TPY* complexes, only the molybdenum and tungsten derivatives with benzene-*o*-dithiolato ligands A^{2-} have been shown to be capable of changing their coordination geometry from trigonal-prismatic to octahedral and *vice versa* depending on the oxidation state of the metal center. A series of mononuclear complexes $[M(bdt)_3]^{n-}$ (M = Mo,[12] W;[13] bdt = benzene-*o*-dithiolate, *n* = 0, 1, 2) has been prepared and characterized by X-ray diffraction. Complex $[W^{VI}(bdt)_3]$[13a] clearly showed a crystallographically imposed perfect trigonal-prismatic coordination geometry at the metal center (Fig. 2). The observed ligand bending at the sulfur atoms is thought to be a consequence of a second-order Jahn–Teller distortion.[14] The one-electron reduction gave the distorted octahedral

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Thorsten Kreickmann was born in Hamm, Germany in 1976. He studied chemistry at the University of Münster where he completed his diploma thesis in Analytical Chemistry in 2002. He joined the Hahn group in 2002. There he developed synthetic routes to bis-(benzene-o-dithiol) ligands and studied their coordination chemistry funded by a stipend of the NRW Graduate School of Chemistry, Münster. After graduation with a Dr. rer. nat. degree in 2005 he was awarded an Alexander von Humboldt Feodor Lynen Fellowship and started in 2006 his postdoctoral studies at the Massachusetts Institute of Technology in the laboratory of Prof. R. Schrock.

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Departments of Chemistry in 1982 (MS, University of Oklahoma), 1983 (Dipl.-Chem., Technische Universität Berlin) and 1985 (Dr. rer. nat. with Prof. H. Schumann, Technische Universität Berlin). Supported by a NATO postdoctoral fellowship he continued his education in the laboratory of Prof. K. N. Raymond at the University of California Berkeley from 1985 to 1988. In 1988 he returned to the Technische Universität Berlin where he completed his Habilitation in 1990. From 1992 to 1998 he was appointed as an Associate Professor at the Freie Universität Berlin. In 1998 he accepted the position as chair of Inorganic Chemistry at the University of Münster. Hahn's primary research interests are coordination chemistry of dithiolato ligands and the organometallic chemistry of multidentate isocyanides and carbenes.
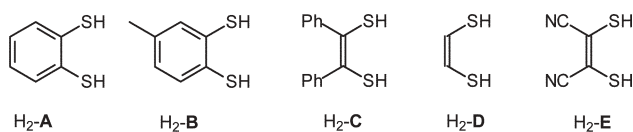
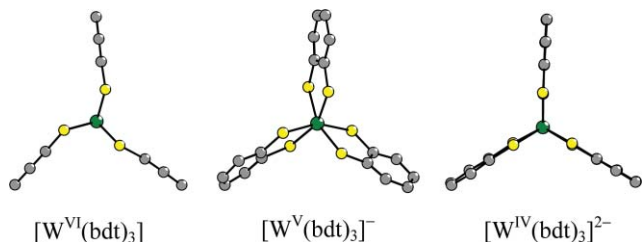Fig. 1 Dithiolato ligands that form trigonal-prismatic complexes.

Fig. 2 Molecular structures of complexes $[W(bdt)_3]^{n-}$ ($n = 0, 1, 2$).

complex anion $[W^{V}(bdt)_3]^{-}$.[13b] Two molecular structures have been reported for $[W^{IV}(bdt)_3]^{2-}$, both exhibiting a more or less distorted trigonal-prismatic coordination geometry.[13c] This indicates that the energy required to modify the twist angle ϕ is small and factors different from the d-electron count at the metal center may influence the coordination geometry. A recent study on the influence of the counter cations on the coordination geometry of 3,6-dichlorobenzene-1,2-dithiolato complexes of tungsten and molybdenum corroborates this assumption.[15] The situation is further complicated by the non-innocent nature of the bdt[2-] ligand. Wieghardt and co-workers have shown, that an intramolecular redox reaction can convert coordinated bdt[2-] into a coordinated *o*-dithio-benzosemiquinonate(1–) radical anion. Under such conditions the *spectroscopic oxidation state* of a metal center may differ from the *formal oxidation state*. The geometrical changes within the ligand associated with such intramolecular redox reactions have been outlined for some hexacoordinated[12c] and tetracoordinated square-planar complexes.[16]

A change of the coordination geometry was also observed during redox reactions with manganese complexes containing two toluene-3,4-dithiolato ligands $\mathbf{B}^{2-}$. The tetrahedral complex $[Mn^{II}(\mathbf{B})_2]^{2-}$ was converted into the square-planar complex $[Mn^{III}(\mathbf{B})_2]^{-}$ by a formal one-electron oxidation.[17]

Regardless of the ultimate reasons, a geometry change was observed for a series of homologous tris(benzene-*o*-dithiolato) complexes in dependence of the *formal oxidation state* of the metal center. We became interested in transferring this feature to dinuclear complexes with bis(benzene-*o*-dithiolato) ligands. Related dicatechol ligands have been known for some time and have been widely used in supramolecular chemistry for the preparation of several structural motifs. Particularly dinuclear triple-stranded helicates M_2L_3[18] and tetranuclear clusters M_4L_6[19] have been prepared with dicatecholato ligands L^{4-} and have been used as catalysts and host molecules for various applications.

Bis(benzene-*o*-dithiol) ligands have been unknown until 1995. We developed a synthesis of such ligands starting from benzene-*o*-dithiol.[20] Subsequently, this method was improved[21] and modified to start with 1,2-di(isopropylmercapto)benzene 1 (Scheme 1), which can be obtained from
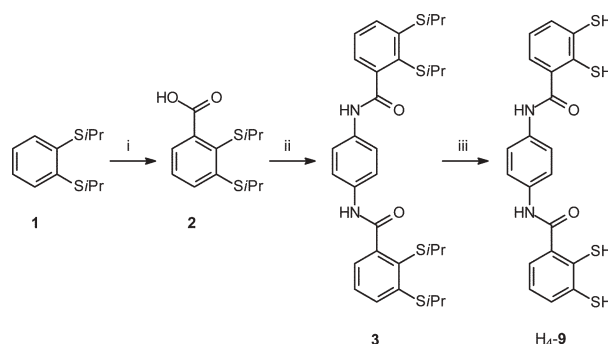
Scheme 1 Synthesis of ligand H4-9. *Reagents and conditions*: (i) (1) *n*BuLi/TMEDA, (2) CO2, (3) HCl–H2O; (ii) (1) SOCl2, (2) *p*-phenylenediamine, NEt3; (iii) (1) Na/naphthalene, (2) HCl–H2O.

1,2-dichlorobenzene and sodium isopropylthiolate.[22] Compound 1 was *ortho*-lithiated and reacted with CO2 which after acidic work-up gave the carboxylic acid 2. Activation of the carboxylic acid 2 with SOCl2 followed by reaction with 0.5 equiv. of a diamine yielded the tetra-S-alkylated ligands. The reaction with 1,4-phenylenediamine is exemplarily shown in Scheme 1. The isopropyl protection groups of compound 3 were removed with sodium/naphthalene in THF or with sodium in liquid ammonia, respectively. Hydrolysis with HCl–H2O gave the moderately air-sensitive bis(benzene-*o*-dithiol) ligand H4-9.

The reaction sequence depicted in Scheme 1 was used for the preparation of the series of bis(benzene-*o*-dithiol) ligands H4-4–H4-11 (Fig. 3). The use of a tripodal triamine such as 1,3,5-diaminomethyl-2,4,6-trimethylbenzene instead of a diamine lead to the tripodal tris(benzene-*o*-dithiol) ligand H6-12.[20a,23]

Apart from ligands containing exclusively benzene-*o*-dithiol groups, we developed a method for the preparation of the mixed benzene-*o*-dithiol/catechol ligands H4-13–H4-16, which were also derived from compound 2. The coupling of the benzene-*o*-dithiol and the catechol moieties was achieved by employing standard protection group chemistry.[24]

2 Coordination chemistry of bis- and tris(benzene-*o*-dithiol) ligands

2.1 Mononuclear chelate complexes

In principle, polydentate ligands are capable to form several different coordination compounds, depending on the topology of the ligand and the preferred coordination geometry of the metal ion. The bis(benzene-*o*-dithiol) ligands H4-10 and H4-11 with long and flexible backbones for example give mononuclear chelate complexes with Co[III] ions.[25] Complexes (NEt4)[Co(10)] and (NEt4)[Co(11)] can be obtained in simple metathesis reactions from Na4-10 and Na4-11 with CoCl2·6H2O, followed by aerial oxidation. However, this method suffers from the high reactivity of the sodium bis(benzene-*o*-dithiolates). We found that the thermodynamically controlled ligand transfer reaction utilizing (NEt4)2[CoCl4] and halophilic bis(titanocene) complexes of H4-10 and H4-11 are a useful tool for the synthesis of cobalt chelate complexes of the ligands 10[4-] and 11[4-]. The
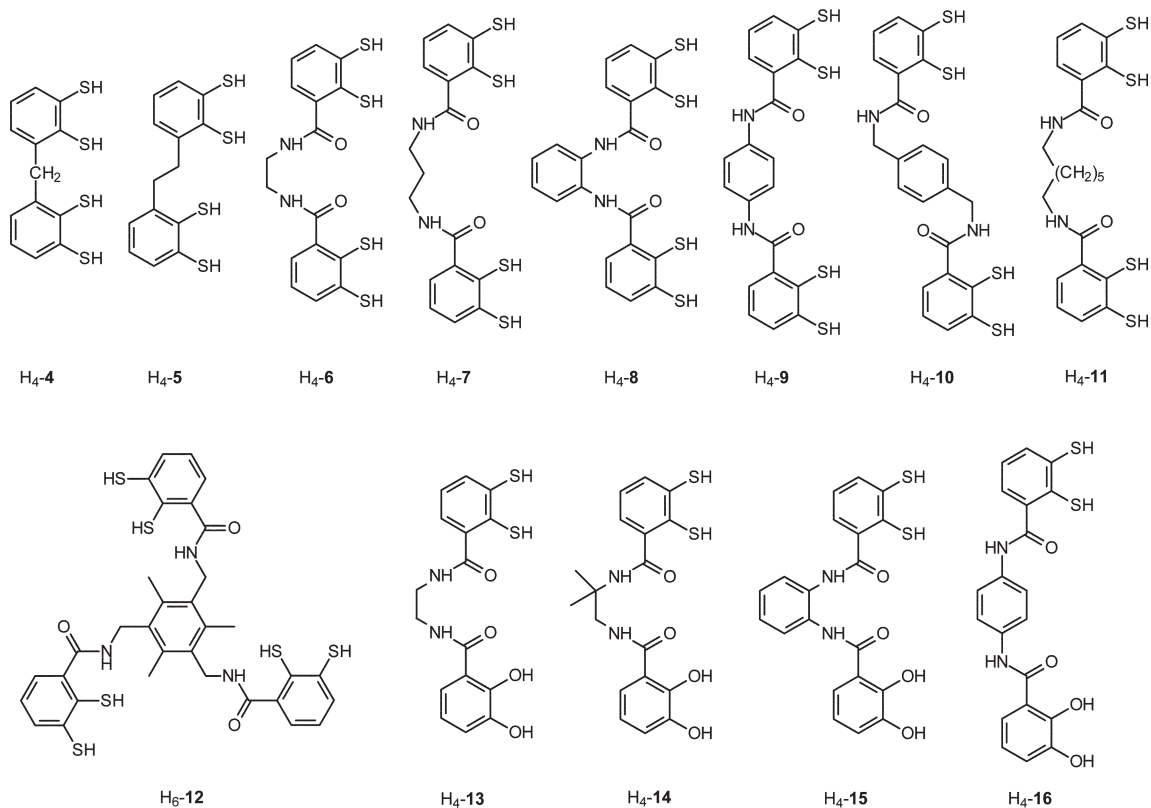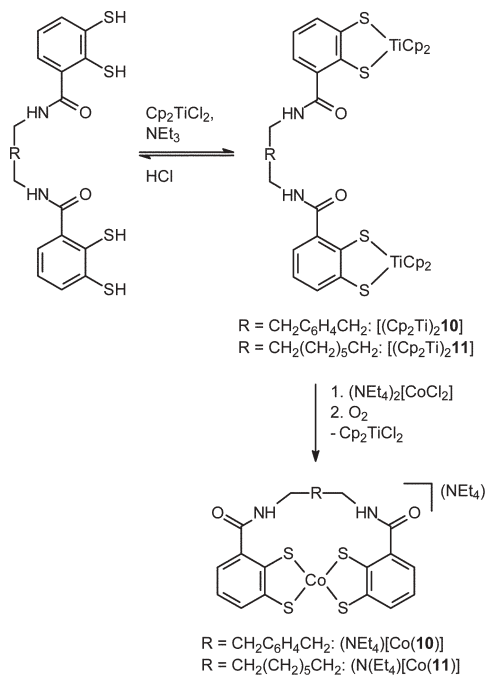
Fig. 3   Polydentate bis(benzene-*o*-dithiol) and benzene-*o*-dithiol/catechol ligands.

bis(titanocene) complexes [(Cp$_2$Ti)$_2$10] and [(Cp$_2$Ti)$_2$11] were obtained from the bis(benzene-*o*-dithiol) ligands H$_4$-10, H$_4$-11 and titanocene dichloride (Scheme 2).[26] This reaction is reversible and protonolysis of the titanocene complexes with

Scheme 2   Synthesis of bis(titanocene) complexes of ligands H$_4$-10 and H$_4$-11 and ligand transfer reaction to cobalt.

HCl reaffords the free ligands. The bis(titanocene) complexes are stable to air and moisture. They are simply purified by column chromatography and subsequent protonolysis in CHCl$_3$ yields the free, air-sensitive bis(benzene-*o*-dithiol) ligands. These are only sparingly soluble in CHCl$_3$ and thus are easily separated from the other reaction product [Cp$_2$TiCl$_2$] which dissolves freely in chloroform.

The isolation of the free bis(benzene-*o*-dithiol) ligands is normally not necessary for complex preparation. The direct reaction of [(Cp$_2$Ti)$_2$10] or [(Cp$_2$Ti)$_2$11] with (NEt$_4$)$_2$[CoCl$_4$] gave complexes (NEt$_4$)[Co(10)] and (NEt$_4$)[Co(11)] after aerial oxidation (Scheme 2). Complex (NEt$_4$)[Co(11)] is stable in solution, while complex (NEt$_4$)[Co(10)] decomposes in acetonitrile solution over a period of several days to yield a solid, which is insoluble in acetonitrile. Since the UV/Vis spectra of both the complex and the decomposition product (in DMF) are very similar, even after four weeks, we assume that complex (NEt$_4$)[Co(10)] probably decomposes in solution to yield a coordination polymer. The UV/Vis spectra of both the complex and the decomposition product resemble that observed for (NEt$_4$)[Co(bdt)$_2$][27] which indicates that the cobalt atom is coordinated in a square-planar fashion in both cases. This coordination geometry was confirmed for complex (NEt$_4$)[Co(11)] in the solid state (Fig. 4, left). The square-planar coordination environment at the cobalt center has previously been observed for the complexes (AsMePh$_3$)[Co(**B**)$_2$],[28] (PMePh$_3$)[Co(**A**)$_2$][29] and (NEt$_4$)[Co-(S$_2$C$_6$Cl$_4$)$_2$][30] with two unbridged benzene-*o*-dithiolato ligands. The electron withdrawing amide groups attached to the aromatic rings lead to the dimerisation of two complex anions
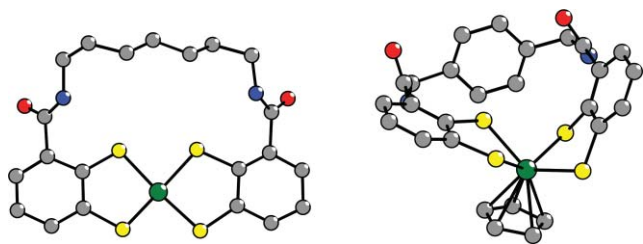
Fig. 4 Molecular structures of the anions [Co(**11**)]⁻ (left) and [(η⁵-C₅H₅)Ti(**10**)]⁻ (right).

[Co(**11**)]⁻, at least in the solid state. This creates two new Co–S bonds, connecting the cobalt atom of one complex anion to a sulfur atom of the adjacent CoS₄ unit. The same type of dimerization has been found for (NEt₄)[Co(S₂C₆Cl₄)₂].[30]

The limited stability of complex (NEt₄)[Co(**10**)] is probably caused by the rigid ligand backbone, that does not permit a strain-free square-planar coordination geometry at the metal center. This assumption is corroborated by the reaction of the dinuclear titanium complex [(Cp₂Ti)₂**10**] (Scheme 2) with NMe₄Cl to give complex (NMe₄)[(η⁵-C₅H₅)Ti(**10**)] (Fig. 4, right).[26] Substitution of at least one benzene-*o*-dithiolato group at one titanium center by chloride ions probably initiates the reaction. Several reaction pathways are conceivable for the following substitution of a cyclopentadienyl ring at the other titanium center by the released benzene-*o*-dithiolate donor[31] and the formal elimination of unstable [(C₅H₅)₃TiCl]. In contrast to the situation in the strained square-planar anion [Co(**10**)]⁻ the two benzene-*o*-dithiolato donors in [(η⁵-C₅H₅)Ti(**10**)]⁻ occupy the basal plane in a square-pyramidal complex anion and are bent into an *exo/endo* conformation relative to the cyclopentadienyl ligand. Owing to the requirements of the bridge the *endo* bend is larger than the *exo* bend, which is the inverse of the situation found in the related anion [(η⁵-C₅H₅)Ti(bdt)₂]⁻ with two unbridged benzene-*o*-dithiolato ligands.[32]

Mononuclear chelate complexes have been obtained from the tris(benzene-*o*-dithiol) ligand H₆-**12**[20a] and metal ions that are capable of coordinating three benzene-*o*-dithiolato units. The catechol analogues of ligand **12**⁴⁻ are well known as highly efficient siderophores, *e.g.* enterobactin which possesses three catechol donor groups linked by a backbone formed from three L-serine units. Ligand H₆-**12** reacts with [Ti(OR)₄] and Li₂CO₃ to give the mononuclear complex Li₂[Ti(**12**)] which after cation exchange with Ph₄AsCl yields (Ph₄As)₂[Ti(**12**)].[23] The structure determination with single crystals of (Ph₄As)₂[Ti(**12**)] (Fig. 5) revealed a distorted

octahedral coordination geometry around the metal center, which is similar to complexes with tricatecholato ligands such as K₂[V(ent)] (H₆ent = enterobactin)[33] and (HNEt₃)[Ti(tripace)] (H₆tripace·HCl = N-centered tripodal tricatechol ligand).[34] The molecular parameters for [Ti(**12**)]²⁻ indicate the unusual presence of intramolecular N–H···S hydrogen bonds, that probably have a structure determining effect such as in the analogous tricatecholylamide complexes.[11,33,35]

2.2 Dinuclear double-stranded complexes

Bis(benzene-*o*-dithiol) ligands with short or inflexible bridging units are no longer capable of forming mononuclear chelate complexes. It is well known that benzene-*o*-dithiolates give square-planar complexes with most metal ions from the first transition period.[36] This observation is also made with bis(benzene-*o*-dithiolato) ligands and thus leads to a large number of dinuclear double-stranded complexes. Ligands H₄-**5** and H₄-**6** form dinuclear double-stranded complexes with Ni^II and, after aerial oxidation, Ni^III and Co^III ions.[21] The molecular structures of complex anions [Ni₂(**5**)₂]⁴⁻ (Fig. 6) and [Ni^II₂(**6**)₂]⁴⁻ (Fig. 7, top) confirm the expected square-planar coordination geometry at the nickel(II) centers. Both Ni^II complex anions are air sensitive and are readily oxidized to the corresponding Ni^III complexes [Ni^III₂(**5**)₂]²⁻ and [Ni^III₂(**6**)₂]²⁻. The X-ray diffraction study for (NEt₄)₂[Ni^III₂(**6**)₂] (Fig. 7, bottom) revealed that the anions
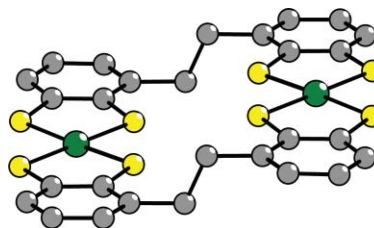
Fig. 6 Molecular structure of the anion [Ni₂(**5**)₂]⁴⁻.

Fig. 5 Molecular structure of the anion [Ti(**12**)]²⁻.
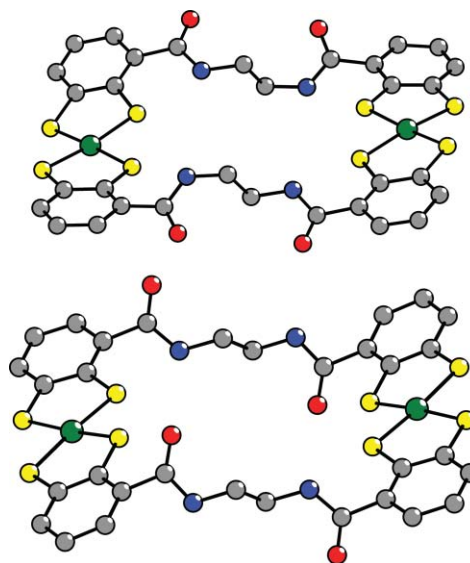
Fig. 7 Molecular structures of the anions [Ni^II₂(**6**)₂]⁴⁻ (top) and [Ni^III₂(**6**)₂]²⁻ (bottom).

$[Ni^{II}_2(\mathbf{6})_2]^{4-}$ and $[Ni^{III}_2(\mathbf{6})_2]^{2-}$ possess similar structures with the exception that all amide NH protons are directed towards the sulfur donor groups in complex $[Ni^{II}_2(\mathbf{6})_2]^{4-}$ which is indicative of the existence of (weak) N–H⋯S hydrogen bonds while the amide protons in complex $[Ni^{III}_2(\mathbf{6})_2]^{2-}$ apparently are not involved in hydrogen bonds. We attribute this observation to the reduced electron density at the sulfur atoms in complex $[Ni^{III}_2(\mathbf{6})_2]^{2-}$.

Cyclic voltammetry studies with complexes $Na_4[Ni_2(\mathbf{5})_2]$ and $(NEt_4)_4[Ni_2(\mathbf{6})_2]$ showed that the bridging unit has a strong influence on the electronic properties of the metal centers. Both complexes show quasi-reversible two-electron transfer waves for the reduction $Ni^{III} \rightarrow Ni^{II}$ with peak potentials recorded at -785 mV for $(NEt_4)_4[Ni_2(\mathbf{6})_2]$ and -1160 mV for $Na_4[Ni_2(\mathbf{5})_2]$ vs. Fc/Fc$^+$. These differences are in accordance with the electron withdrawing character of the diamide bridge in $[Ni_2(\mathbf{6})_2]^{2-}$ and the electron-donating character of the alkyl bridge in $[Ni_2(\mathbf{5})_2]^{2-}$ which make the latter complex more difficult to reduce.

In their search for model compounds for iron only nitrogenase, Sellmann et al. investigated the reaction of ligand H$_4$-$\mathbf{7}$ with iron(III) ions. A dinuclear double-stranded complex $(AsPh_4)_2[Fe_2(\mathbf{7})_2]$ was obtained which differs significantly from that of the dinuclear nickel complexes.[37]

The anion $[Fe_2(\mathbf{7})_2]^{2-}$ contains two FeS$_4$ units that are linked by two Fe–S–Fe bridges leading to two distorted square pyramidal, five coordinate iron centres (Fig. 8). A similar coordination mode has been observed in complexes $(NEt_4)[Fe(\mathbf{A})_2]$[38] and $(NBu_4)[Fe(\mathbf{B})_2]$[39] with unbridged benzene-o-dithiolato donor units. We take this as an indication that the bridging of two FeS$_4$ units is not a consequence of the linking of two benzene-o-dithiol units. However, the peripheral ligand bridges prevent a complete separation of the $[Fe(S_2C_6H_3R)_2]$ entities, which is observed for complexes $(NEt_4)[Fe(\mathbf{A})_2]$ and $(NBu_4)[Fe(\mathbf{B})_2]$ in solution by interactions of the anions with the solvent molecules.

The carboxamide subunits in $[Fe_2(\mathbf{7})_2]^{2-}$ can adopt a configuration that is in plane with or orthogonal to the benzene ring. The configuration found in solvent-free crystals of $(AsPh_4)_2[Fe_2(\mathbf{7})_2]$ (Fig. 8) seems to be arbitrary since the molecular structure revealed different orientations with regard to the benzene rings. Obviously N–H⋯S hydrogen bonds do not have a structure determining effect in this type of complex.

No dinuclear double or triple-stranded complexes have been obtained with ligand H$_4$-$\mathbf{4}$ and Ni^{II} or Co^{III} ions, although the ligand topology should in principle allow the formation of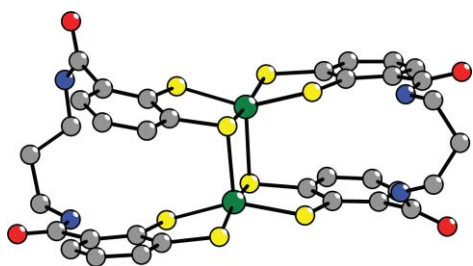 such complexes. For example, the homologous dicatechol ligand has been shown to yield a triple-stranded helicate with Ti^{IV}.[18g] Instead, the tetranuclear complex anion $[Co_4(\mathbf{4})_4]^{4-}$ has been obtained in the reaction of H$_4$-$\mathbf{4}$ with CoCl$_2$·6H$_2$O followed by aerial oxidation.[40] The molecular structure of $(PNP)_4[Co_4(\mathbf{4})_4]$ (Fig. 9) revealed that a metallamacrocycle with two differently coordinated cobalt centers had formed in the solid state. The preparation of a double- or triple-stranded helicate is not possible with H$_4$-$\mathbf{4}$ as the longer Co–S and C–S bonds in such a complex would lead to short non-bonding intrastrand S⋯S contacts, a feature which is of no significance in the homologous complex with the dicatecholato ligand.[40] Two cobalt atoms in $[Co_4(\mathbf{4})_4]^{4-}$ are coordinated by benzene-o-dithiolato units with their alkyl substituents arranged in anti position, while the other two cobalt atoms are coordinated by benzene-o-dithiolato units with the alkyl substituents in syn position. As a result, the molecular anion possesses two different C_2 axes.

In search for dinuclear triple-stranded helicates we reacted ligand H$_4$-$\mathbf{8}$ with $[Ti(OC_2H_5)_4]$ and Li$_2$CO$_3$ in methanol. This reaction did not lead to the formation of a triple-stranded helicate $[Ti_2(\mathbf{8})_3]^{4-}$. Instead, the dinuclear double-stranded complex $[Ti_2(\mathbf{8})_2(\mu\text{-OCH}_3)_2]^{2-}$ was obtained.[41] The single crystal X-ray diffraction analysis of $(Ph_4As)_2[Ti_2(\mathbf{8})_2(\mu\text{-OCH}_3)_2]$ revealed that the two metal centers are connected by two ligand strands $\mathbf{8}^{4-}$ in addition to two methoxo ligands which are part of a central four-membered $Ti_2(\mu\text{-OCH}_3)_2$ ring (Fig. 10). The coordination geometry at the metal centers is best described as strongly distorted octahedral. The anion $[Ti_2(\mathbf{8})_2(\mu\text{-OCH}_3)_2]^{2-}$ resides on a crystallographic inversion center. Therefore the two titanium atoms must assume different configurations (Λ and Δ) which leads to a meso-complex. The non-bonding intramolecular N⋯S distances are long (range 3.577 and 3.643 Å) and the amide group and the attached benzene-o-dithiolate group are not coplanar, which excludes the presence of strong intramolecular N–H⋯S hydrogen bonds. The absence of such hydrogen bonds was also indicated by the ^{1}H NMR spectra of $(Ph_4As)_2[Ti_2(\mathbf{8})_2(\mu\text{-OCH}_3)_2]$ where the resonance for the amide protons was observed only slightly upfield from the same resonance for the free ligand H$_4$-$\mathbf{8}$. A bonding situation similar to the one in $[Ti_2(\mathbf{8})_2(\mu\text{-OCH}_3)_2]^{2-}$ has been found for the titanium(IV) complex with the homologous dicatecholato ligand. However, in this dinuclear double-stranded complex strong intramolecular N–H⋯O hydrogen bonds exist.[41]
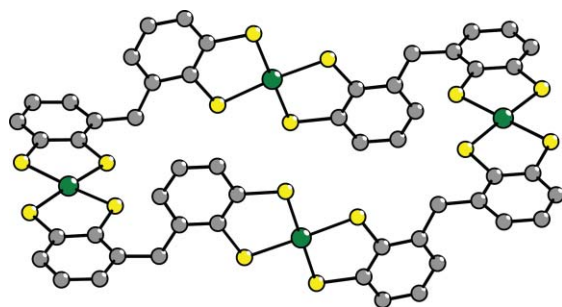

Fig. 8 Molecular structure of the anion $[Fe_2(\mathbf{7})_2]^{2-}$.

Fig. 9 Molecular structure of the anion $[Co^{III}_4(\mathbf{4})_4]^{4-}$.

2.3 Dinuclear triple-stranded helicates

Metallohelicates belong to the most thoroughly studied compounds in supramolecular chemistry and an enormous amount of such complexes with N- and O-donors has been prepared.[42] Particularly dicatechol ligands have found much interest, since they are potential analogues of siderophores such as rhodotorulic acid.[43] However, the majority of the dicatechol ligands has been used for the preparation of metallohelicates.[44]

The first triple-stranded helicates with bis(benzene-*o*-dithiolato) ligands have been obtained only recently with ligands H$_4$-**6** and H$_4$-**9**. The reaction of [Ti(OC$_2$H$_5$)$_4$] with these ligands in the presence of Li$_2$CO$_3$ yields the dark red compounds Li[Ti$_2$(**6**)$_3$] and Li$_4$[Ti$_2$(**9**)$_3$].[41,45] The alkali metal salts have been found difficult to crystallize and therefore the salt metathesis reaction with (PNP)Cl has been carried out to give the complexes Li(PNP)$_3$[Ti$_2$(**6**)$_3$] and (PNP)$_4$[Ti$_2$(**9**)$_3$] in pure, crystalline form. It should be noted, that the exchange of the remaining lithium cation in Li(PNP)[Ti$_2$(**6**)$_3$] could not be achieved, even when a large excess of (PNP)Cl was used in the metathesis reaction.[41,45]

The triple-stranded helical anions [Ti$_2$(**6**)$_3$]$^{4-}$ and [Ti$_2$(**9**)$_3$]$^{4-}$ show very simple ^{1}H NMR spectra with only one set of signals for the protons for the three ligand strands, indicating C_3 symmetry for the complex anions in solution. The signals for the amide protons in the complex anions are shifted downfield relative to H$_4$-**6** ($\Delta\delta$ = 0.85 ppm) and H$_4$-**9** ($\Delta\delta$ = 0.53 ppm), respectively. This indicates the presence of N–H$\cdots$S hydrogen bonds in a six-membered ring between the amide protons and the *o*-thiolato sulfur atoms. So far, similarly strong N–H$\cdots$S hydrogen bonds have only been observed in more stable five-membered rings.[46]

Compounds Li(PNP)$_3$[Ti$_2$(**6**)$_3$] and (PNP)$_4$[Ti$_2$(**9**)$_3$] crystallized as racemic mixtures of the $\Lambda\Lambda$ and $\Delta\Delta$ isomers in centrosymmetric space groups. The molecular structures of the anions [Ti$_2$(**6**)$_3$]$^{4-}$ ($\Delta\Delta$ isomer) and [Ti$_2$(**9**)$_3$]$^{4-}$ ($\Lambda\Lambda$ isomer) are depicted in Fig. 11. The molecular structure of the anion [Ti$_2$(**9**)$_3$]$^{4-}$ resembles the one reported by Raymond and co-workers[18c] for the dinuclear triple-stranded helicate with the corresponding dicatecholato ligand.

Short nonbonding intraligand N$\cdots$S distances between the amide nitrogen atoms and the *ortho*-sulfur atoms of the adjacent benzene-*o*-dithiolato groups are found in both helical anions. The benzene-*o*-dithiolato and the amide subunits are arranged in a nearly coplanar fashion. The observation of a small dihedral angle between these groups supports the
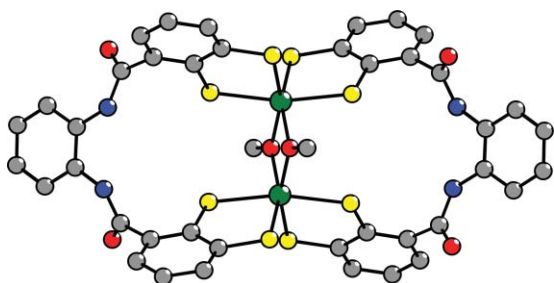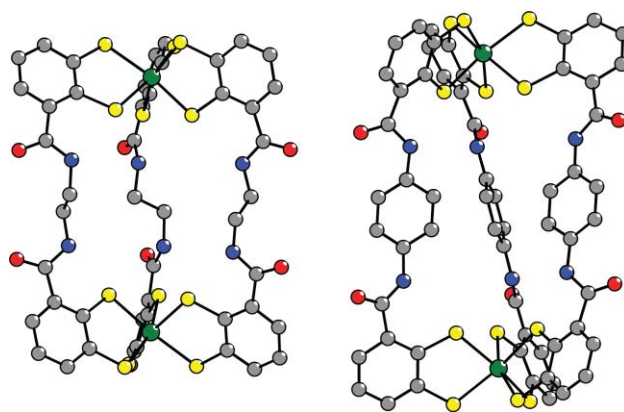

Fig. 10 Molecular structure of the anion [Ti$_2$(**8**)$_2$(μ-OCH$_3$)$_2$]$^{2-}$.

Fig. 11 Molecular structures of the anions [Ti$_2$(**6**)$_3$]$^{4-}$ (left) and [Ti$_2$(**9**)$_3$]$^{4-}$ (right).

existence of strong N–H$\cdots$S hydrogen bonds. Their presence was confirmed by ^{1}H NMR spectroscopy. As a consequence, the Ti–S bond lengths to the sulfur atoms in *ortho*-position to the amide functions are elongated, while the Ti–S bond lengths to the sulfur atoms in *meta*-position are shorter.[41]

The lithium cation in crystals of compound Li(PNP)$_3$[Ti$_2$(**6**)$_3$]·3DMF·H$_2$O is coordinated by two carbonyl groups of two different anions [Ti$_2$(**6**)$_3$]$^{4-}$ and by a water and a DMF molecule in the asymmetric unit. This leads to indefinite polymeric chains Li–[Ti$_2$(**6**)$_3$]$^{4-}$–Li–[Ti$_2$(**6**)$_3$]$^{4-}$ in the crystal lattice (Fig. 12). In contrast to this, the [Ti$_2$(**9**)$_3$]$^{4-}$-anions in compound (PNP)$_4$[Ti$_2$(**9**)$_3$]·3DMF are well separated with no interactions between cations and anions.[41] The helical twist angles[47] in both complex anions differ significantly. The rigid ligand **9**$^{4-}$ in the complex anion [Ti$_2$(**9**)$_3$]$^{4-}$ leads to a twist angle of 60° while the more flexible ligand **6**$^{4-}$ in the complex anion [Ti$_2$(**6**)$_3$]$^{4-}$ causes a comparatively small twist angle of only 12°.

NMR spectroscopic investigations showed that the coordination mode of the lithium cation is maintained in solution, but a dynamic process must be assumed in which all carbonyl groups contribute to the coordination environment of the lithium cation.

3 Coordination chemistry of benzene-*o*-dithiol/catechol ligands

3.1 Dinuclear double-stranded complexes

Tetradentate ligands with different donor groups such as benzene-*o*-dithiol/catechol derivatives (directional ligands)[48,49] are of special interest, since they offer the opportunity to prepare heterodinuclear complexes as well as complexes with a different orientation of the ligand strands. The versatile coordination chemistry of bis(benzene-*o*-dithiol) ligands described in section 2 prompted us to substitute one of the benzene-*o*-dithiol groups for a catechol group, leading to ligands H$_4$-**13**–H$_4$-**16** (Fig. 3).

In order to investigate the coordination chemistry of mixed benzene-*o*-dithiol/catechol ligands we reacted ligand H$_4$-**13** with [TiO(acac)$_2$] and Na$_2$CO$_3$. Since the bis(benzene-*o*-dithiol) ligand H$_4$-**6** (Fig. 11) and its catechol homologue[44]
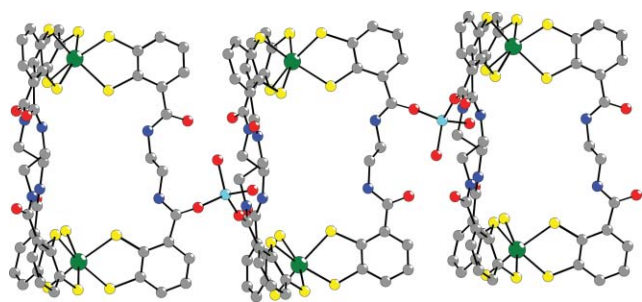
Fig. 12 Partial view of the polymeric chains in the crystal lattice of Li(PNP)[Ti$_2$(**6**)$_3$]·3DMF·H$_2$O. No PNP$^+$ cations and only the oxygen atoms of the solvent molecules coordinating to the bridging lithium cation are shown.

with the same topology as H$_4$-**13** both form dinuclear triple-stranded helicates [Ti$_2$L$_3$]$^{4-}$ we expected the formation of a triple-stranded helicate Na$_4$[Ti$_2$(**13**)$_3$]. Surprisingly, all attempts to prepare the triple-stranded complex anion [Ti$_2$(**13**)$_3$]$^{4-}$ failed and the double-stranded complex Na$_2$[Ti$_2$(**13**)$_2$(μ-OCH$_3$)$_2$] was exclusively obtained.[50]

The directionality of the ligand **13**$^{4-}$ enables the formation of two regioisomeric complex anions [Ti$_2$(**13**)$_2$(μ-OCH$_3$)$_2$]$^{2-}$, one with a parallel orientation of the ligand strands and one with an antiparallel orientation. In addition, the chirality at the metal centers allows the generation of up to seven stereoisomers (Fig. 13). Since ligand H$_4$-**13** is achiral, six of the seven stereoisomers form three pairs of enantiomers.

The ^{1}H NMR spectrum of (Ph$_4$As)$_2$[Ti$_2$(**13**)$_2$(μ-OCH$_3$)$_2$] (*e.g.* the observation of six NH resonances, two for each isomer/pair of enantiomers) showed, that three of the four possible isomers/pairs of enantiomers are formed in solution, which means that at least one isomer with a parallel and one isomer with an antiparallel orientation of the ligand strands is present in solution.

The X-ray analysis of compound (AsPh$_4$)$_2$[Ti$_2$(**13**)(μ-OCH$_3$)$_2$] (Fig. 14). did not provide conclusive results. The
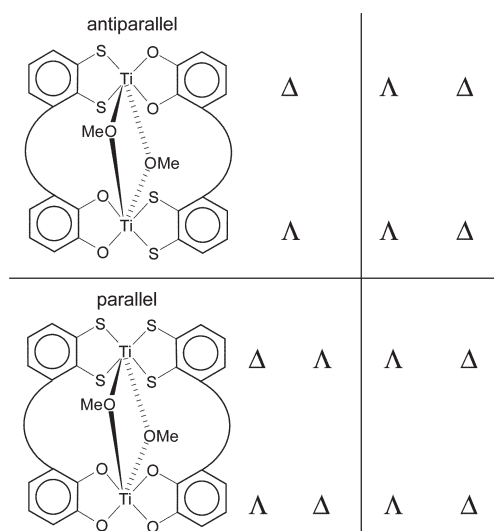
compound crystallized in the centrosymmetric space group $P\bar{1}$ with $Z = 1$. The complex dianion resides on a crystallographic inversion center. Provided that there is no crystallographic disorder, the complex dianion with the parallel orientation of the ligand strands, which is present in solution, cannot lie on an inversion center. The detection of [Ti$_2$(**13**)(μ-OCH$_3$)$_2$]$^{2-}$ on a crystallographic inversion center could therefore indicate that only complex anions with an antiparallel orientation of the ligand stands are present in the crystals of (AsPh$_4$)$_2$[Ti$_2$(**13**)(μ-OCH$_3$)$_2$]. Alternatively, all three isomers present in solution could co-crystallize in a disordered lattice. Unfortunately, the latter situation was observed. The dianion is severely disordered in the solid state. All donor atoms (S and O) coordinated to the titanium atoms are disordered. As a consequence each benzene-*o*-dithiolato group can be replaced with a catecholato group and *vice versa*. Therefore, no unambiguous assignment can be made regarding the donor atoms for each titanium atom and the orientation of the ligand strands cannot be determined.

The crystal structure determination only confirms the chemical composition of the dianion to be [Ti$_2$(**13**)$_2$(μ-OCH$_3$)$_2$]$^{2-}$. One of the possible isomers of the [Ti$_2$(**13**)$_2$(μ-OCH$_3$)$_2$]$^{2-}$ anion present in the crystal is depicted in Fig. 14.[50] This is the isomer with the antiparallel orientation of the ligand strands and opposite configurations at the metal centers corresponding best to the crystallographically observed site symmetry.

The double-stranded complex anion [Ti$_2$(**15**)$_2$(μ-OCH$_3$)$_2$]$^{2-}$ was obtained from [TiO(acac)$_2$] and the *o*-phenylenediamine bridged benzene-*o*-dithiol/catechol ligand H$_4$-**15** in methanol at room temperature.[50] Contrary to the observation for the anion [Ti$_2$(**13**)$_2$(μ-OCH$_3$)$_2$]$^{2-}$, ^{1}H NMR spectroscopy indicated the formation of only one pair of enantiomers in solution. Only the amide protons linked to the catechoylamido groups form strong hydrogen bonds with the catecholato oxygen atoms which leads to a downfield shift of the resonance for these protons in the complex anion relative to the resonance for the free ligand H$_4$-**15**. In contrast to the triple-stranded helical anions [Ti$_2$(**6**)$_3$]$^{4-}$ and [Ti$_2$(**9**)$_3$]$^{4-}$, the formation of N–H···S hydrogen bonds was not observed for complex [Ti$_2$(**15**)$_2$(μ-OCH$_3$)$_2$]$^{2-}$ in solution.

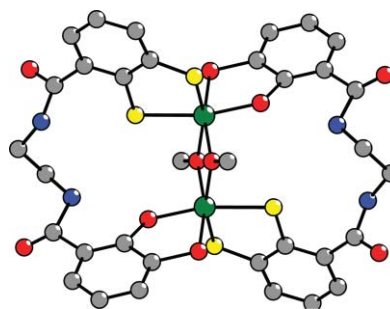Since the orientation of the ligand strands cannot be determined by NMR spectroscopy a crystal structure analysis

antiparallel

| | Δ | Λ | Δ |
| | Λ | Λ | Δ |

parallel

| | Δ | Λ | Λ | Δ |
| | Λ | Δ | Λ | Δ |

Fig. 13 Schematic representation of the possible isomers of the anion [Ti$_2$(**13**)(μ-OCH$_3$)$_2$]$^{2-}$.

Fig. 14 Molecular structure of a centrosymmetric anion [Ti$_2$(**13**)$_2$(μ-OCH$_3$)$_2$]$^{2-}$ present in crystals of (AsPh$_4$)$_2$[Ti$_2$(**13**)$_2$-(μ-OCH$_3$)$_2$]. The color code of the donor groups (S and O) is arbitrary since all donor atoms are disordered.
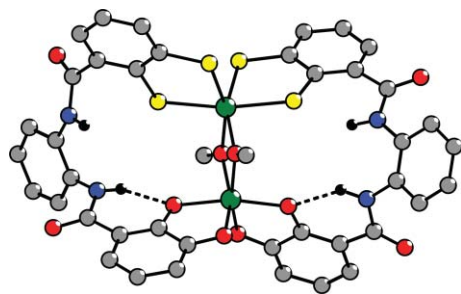
Fig. 15 Molecular structure of the anion $[Ti_2(15)_2(\mu\text{-}OCH_3)_2]^{2-}$.

was carried out with single crystals of $(PNP)_2[Ti_2(15)_2(\mu\text{-}OCH_3)_2]$. It revealed a parallel orientation of the ligand strands (Fig. 15). The reasons for the parallel orientation of the ligand strands is at the moment subject to speculation. It is reasonable to assume, that the formation of strong N–H···O hydrogen bonds, that has been observed in the solid state, has an influence on the orientation of the ligand strands.

When the reaction of H_4-**15** and $[TiO(acac)_2]$ was carried out at elevated temperature in the presence of Na_2CO_3, the initial formation of complex $Na_2[Ti_2(15)_2(\mu\text{-}OCH_3)_2]$ was observed. In the presence of an excess of ligand Na_4-**15** the triple-stranded helicate $Na_4[Ti_2(15)_3]$ formed over a period of 24 h at 50 °C.[50] Among all triple-stranded helicates we studied, $(PNP)_4[Ti_2(15)_3]$ is the only one that is formed as a mixture of two geometrical isomers in solution. We assigned this behaviour to the elevated reaction temperature. ^{1}H NMR investigations showed that the isomers with a parallel orientation and with an antiparallel orientation of the ligand strands coexist in solution.

Fig. 16 displays the two isomers and the ^{1}H NMR spectrum of $(PNP)_4[Ti_2(15)_3]$. The two geometrical isomers have been identified by the appearance of six triplets that can be assigned to the six different protons of the donor groups in *meta*-position to the amide groups. An integration analysis showed
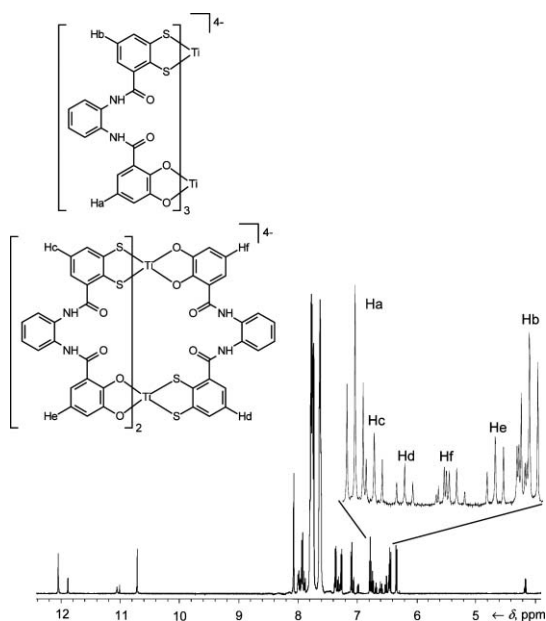

Fig. 16 ^{1}H NMR spectrum of complex $(PNP)_4[Ti_2(15)_3]$.

that the triple-stranded helicate with the parallel orientation of the ligand strands is the major product (65%).

3.2 Dinuclear triple-stranded complexes

Ligands H_4-**14** and H_4-**16** react with $[TiO(acac)_2]$ and Na_2CO_3 in methanol to give exclusively the triple-stranded helicates $Na_4[Ti_2(14)_3]^{24,50}$ and $Na_4[Ti_2(16)_3]$.[50] Attempts to prepare a dinuclear double-stranded complex $Na_2[Ti_2(14)_2(\mu\text{-}OCH_3)_2]$ related to $Na_2[Ti_2(13)_2(\mu\text{-}OCH_3)_2]$ (Fig. 14) failed, although H_4-**14** and H_4-**13** have the same ligand backbone, except the methyl groups of the bridging unit in H_4-**14**. Attempts to exchange all four sodium cations by PNP^+ cations failed in both cases even after addition of up to 10 equivalents of $(PNP)Cl$ to methanolic solutions of $Na_4[Ti_2(14)_3]$ and $Na_4[Ti_2(16)_3]$. Only three sodium cations could be exchanged, resulting in the formation of complexes $Na(PNP)_3$-$[Ti_2(14)_3]^{24,50}$ and $Na(PNP)_3[Ti_2(16)_3]$.[50]

^{1}H NMR spectra of $Na(PNP)_3[Ti_2(14)_3]^{24,50}$ showed only one set of signals for the ligand strands ($2 \times$ t, $4 \times$ d for the aromatic protons) which demonstrated the exclusive formation of the geometrical isomer with a parallel orientation of the ligand strands. A strong downfield shift of the catechoylamide NH proton in $[Ti_2(14)_3]^{4-}$ relative to the free ligand H_4-**14** indicates the formation of strong N–H···O hydrogen bonds, whereas no N–H···S hydrogen bonds were detected in the $[Ti_2(14)_3]^{4-}$ anion. While NMR spectroscopy showed, that only one pair of stereoisomers ($\Lambda\Delta/\Delta\Lambda$ or $\Lambda\Lambda/\Delta\Delta$) is present in solution, an X-ray diffraction study was carried out to show that both metals in $[Ti_2(14)_3]^{4-}$ adopt the same absolute configuration (Fig. 17, left). Upon crystallization spontaneous resolution into crystals containing exclusively the $\Lambda\Lambda$ or the $\Delta\Delta$ isomer (space group $P1$) occurred. The unit cell of $Na(PNP)_3[Ti_2(14)_3]$ contains one tetraanion $[Ti_2(14)_3]^{4-}$, three PNP^+ cations, one sodium cation and one molecule of water, methanol and diethyl ether each. The sodium cation acts as a bridge between two $[Ti_2(14)_3]^{4-}$ tetraanions by coordination of amide carbonyl functions of two different tetraanions and this leads to indefinite polymeric chains Na–$[Ti_2(14)_3]^{4-}$–Na–$[Ti_2(14)_3]^{4-}$ in the crystal lattice similar to those found for $Li(PNP)[Ti_2(6)_3]^{41,45}$ (Fig. 12).

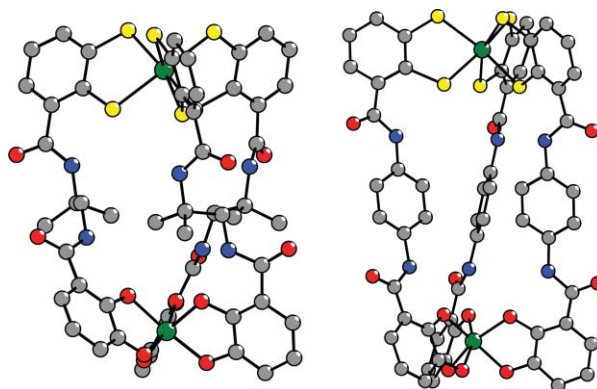Reaction of three equivalents of H_4-**16** with two equivalents of $[TiO(acac)_2]$ and Na_2CO_3 in methanol at room temperature

Fig. 17 Molecular structures of the anions $[Ti_2(14)_3]^{4-}$ (left) and $[Ti_2(16)_3]^{4-}$ (right).

under an argon atmosphere gave a deep red solution of $Na_4[Ti_2(16)_3]$.[50] As was observed with $Na_4[Ti_2(14)_3]$[24] only three of the four sodium cations can be substituted with PNP^+ cations. The ligand strands in $Na(PNP)_3[Ti_2(16)_3]$ are oriented in the parallel fashion (Fig. 17, right) and strong $N–H\cdots O$ hydrogen bonds were detected by ^1H NMR spectroscopy in solution and in the solid state. In contrast to the situation in $Na(PNP)_3[Ti_2(14)_3]$, two tetraanions $[Ti_2(16)_3]^{4-}$ are connected via a sodium cation that is coordinated by the three meta oxygen atoms of the catecholato groups of each complex tetraanion thereby forming a central NaO_6 octahedron in an anionic pentanuclear complex $\{[Ti_2(14)_3]–Na–[Ti_2(14)_3]\}$.[50]

4 Conclusion and outlook

We have prepared a series of bis(benzene-o-dithiol) and mixed benzene-o-dithiol/catechol ligands and studied their coordination chemistry. Some analogies to the homologous dicatechol ligands were found. However, the binding properties of the benzene-o-dithiolate donor group together with the observation that tungsten and molybdenum complexes of type $[M(bdt)_3]^{n-}$ exhibit a coordination geometry which depends on the d-electron number of the metal might give access to unique supramolecular compounds in the future. The preparation of heterodinuclear helicates, for example with tungsten and titanium, should be facile with mixed benzene-o-dithiol/catechol ligands exploiting the different binding preferences of the donor groups (Scheme 3). The variation of the metal oxidation states can then be used to control the coordination geometry of the TiO_6 and WS_6 polyhedra. While the TiO_6 moiety is most likely an octahedron with the titanium atom coordinated by six catecholato oxygen atoms, the coordination geometry of the $W(bdt)_3$ polyhedron might be changed from trigonal-prismatic for W^{VI} to distorted octahedral for W^V. This would, in principle, allow to switch off or on the helicity of a heterodinuclear complex by a redox reaction at the WS_6 polyhedron. In addition, the redox induced geometry changes at the WS_6 polyhedron might require additional energy to change the conformation of the backbone which could be stored and released in the back-reaction.

The different binding preferences of mixed benzene-o-dithiol/catechol ligands can also be used to generate very large supramolecular architectures. Raymond an co-workers have shown that modifications of the linker between two catechol groups will give ligands which do not form helicates
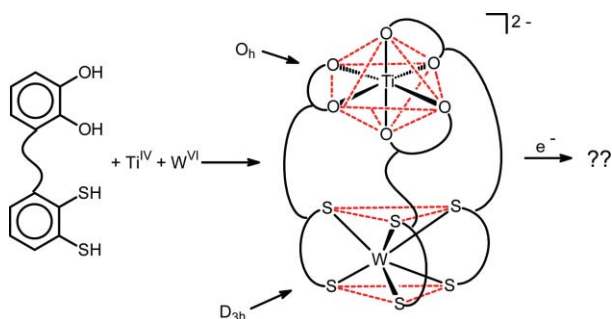
Scheme 3 Preparation of heterobimetallic helicates from benzene-o-dithiol/catechol ligands.
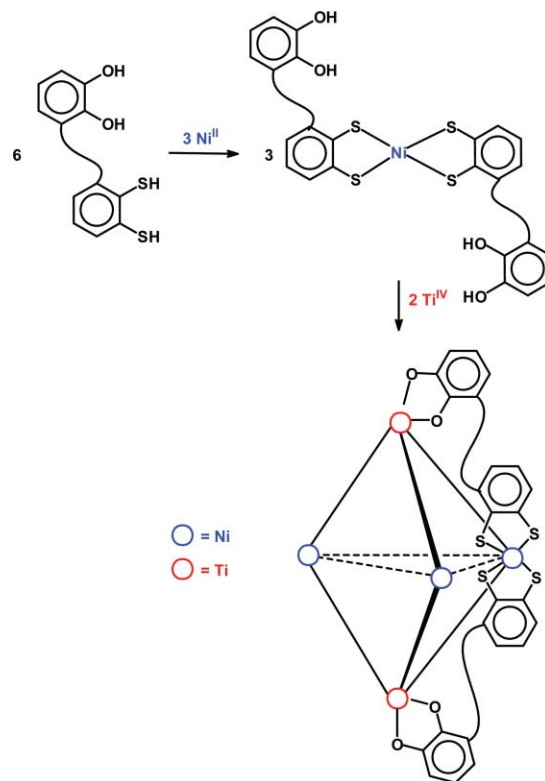
Scheme 4 Assembly of heterodinuclear trigonal-bipyramidal clusters with mixed benzene-o-dithiol/catechol ligands.

of type $[M_2L_3]^{n-}$ but instead react with selected metal ions to give large tetrahedral clusters of composition $[M_4L_6]^{n-}$.[19] Such clusters have been used successfully as "molecular flasks" for selected transformations.[19c–f] While clusters with a different geometry (e.g. trigonal-bipyramidal) can be envisioned by further modifications at the bridging unit between the catechol donors, they have been elusive so far. Mixed benzene-o-dithiol/catechol ligands might allow the preparation of heterobimetallic trigonal-bipyramidal clusters again by utilizing the different binding preferences of the donor groups. If a mixed benzene-o-dithio/catechol ligand is reacted with Ni^{II} the square-planar NiS_4 complex will be obtained (Scheme 4). Reaction of three equivalents of such a complex with two equivalents of Ti^{IV} could lead to a trigonal-bipyramidal supramolecular complex containing three square-planar Ni^{II} and two octahedral Ti^{IV} metal centers (Scheme 4). Modeling studies have shown that the yet unknown ligand with a 1,3-phenylenediamide backbone is best suited for the preparation of such a supramolecular assembly. Preparative studies towards the synthesis of trigonal-bipyramidal mixed metal clusters with suitable benzene-o-dithiolato/catecholato ligands and their use as molecular reaction vessels for selected substrates are currently in progress.

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