Helical Structures

DOI: 10.1002/anie.200801172

# Heterobimetallic Triple-Stranded Helicates with Directional Benzene-*o*-dithiol/Catechol Ligands**

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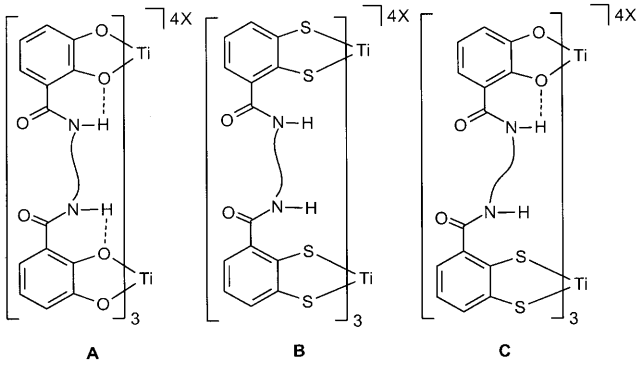
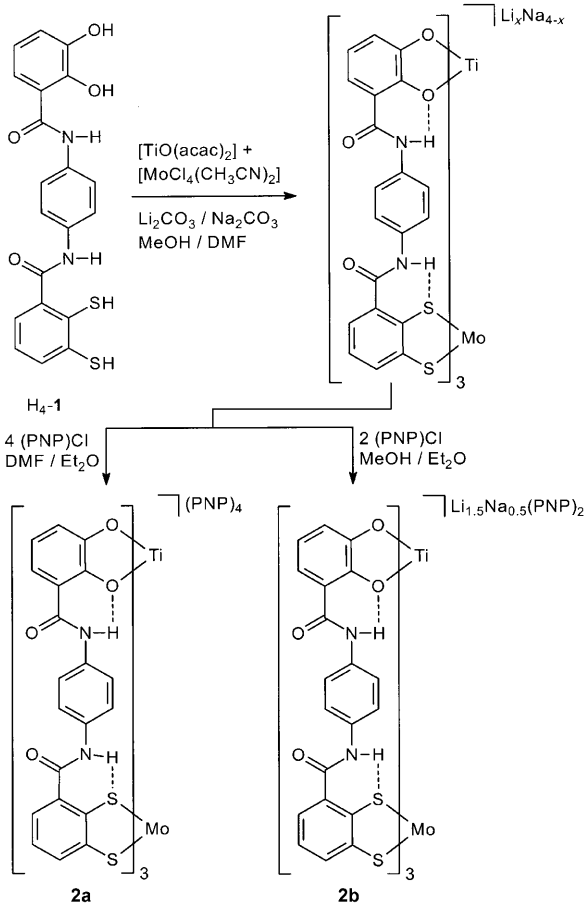
In recent years, the coordination chemistry of metallohelicates has developed into a steadily expanding field of metallosupramolecular chemistry.[1] A large number of helical complexes with bidentate nitrogen[2] or catecholato donor groups[3] (**A**, Scheme 1) have been presented. A first application of such complexes has been described for a dinuclear, triple-stranded iron(II) helicate, which binds in the major groove of DNA, causing intramolecular DNA coiling.[4] Much less is known about supramolecular complexes with the benzene-*o*-dithiolato donor group.[5] Even though the ligand topology is similar to the catecholato group, its electronic features are clearly different. We have recently reported the self-assembly of dinuclear triple-stranded helicates **B** from three bis(benzene-*o*-dithiolato) ligands and two titanium(IV) ions.[6] The connection of benzene-*o*-dithiolato and catecholato units leads to new diamide-bridged directional (S–S/O–O) ligands, which are capable of forming homobimetallic helical complexes **C** with parallel ligand strands.[7]




***Scheme 1.*** Helical complexes of types **A**–**C**.

We have now started to use the different binding preferences of the donor groups in mixed benzene-*o*-dithiol/catechol ligands for the selective assembly of heterobimetallic helical complexes. Herein we describe the syntheses of the first heterobimetallic triple-stranded helicates $(PNP)_4[TiMo(\mathbf{1})_3]$ (**2a**, PNP = bis(triphenylphosphoranylidene)ammonium) and $Li_{1.5}Na_{0.5}(PNP)_2[TiMo(\mathbf{1})_3]$ (**2b**) with the directional benzene-*o*-dithiol/catechol ligand $H_4$-**1** (Scheme 2) and discuss the influence of the cations $Li^+$, $Na^+$, and $PNP^+$ on the configuration and coordination mode of the $\{Ti^{IV}O_6\}$ and $\{Mo^{IV}S_6\}$ polyhedra in these complexes.

Directional ligands are obtained when a symmetric spacer bridges two different donor groups[8] as in $H_4$-**1** or when two identical donor groups such as catechol are bridged by an asymmetric spacer.[9] Dinuclear triple-stranded helicates with




***Scheme 2.*** Syntheses of the heterobimetallic helicates $(PNP)_4[TiMo(\mathbf{1})_3]$ (**2a**) and $Li_{1.5}Na_{0.5}(PNP)_2[TiMo(\mathbf{1})_3]$ (**2b**); acac = acetylacetonate.

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[**] Financial support for this work was provided by the Deutsche Forschungsgemeinschaft (IRTG 1444).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200801172.

such ligands are obtained as different enantiomers (Λ- or Δ-isomers). Moreover, regioisomeric complexes can be formed in which the ligands are arranged in a parallel or antiparallel orientation.[7,10] For example, the reaction of a directional mixed catecholato/aminophenolato ligand with either $Ga^{III}$ or $Ti^{IV}$ yields exclusively the homodinuclear complex with antiparallel ligands, whereas the reaction with a mixture of $Ga^{III}$ and $Ti^{IV}$ (1:1) leads to a heterodinuclear complex with parallel ligand strands.[8a] Furthermore, the regioselective aggregation of heterobimetallic triple-stranded helicates can be controlled by the reaction of segmental ligands containing bi- and tridentate binding groups with suitable d- ($Co^{II}$, $Cr^{II}$) and f-block ($La^{III}$, $Lu^{III}$) metal ions. The heterobimetallic complexes obtained in this manner exhibit remarkable photophysical properties.[8b] The first directional benzene-*o*-dithiol/catechol ligand that contains an unsymmetrical spacer reacts with $Ti^{IV}$ under exclusive formation of a homodinuclear triple-stranded helicate (**C** in Scheme 1) with a parallel orientation of the three ligand strands.[7]

We are now attempting to selectively synthesize heterodinuclear $Ti^{IV}/Mo^{IV}$ helicates with a parallel orientation of the ligand strands utilizing the different binding preferences in the mixed benzene-*o*-dithiol/catechol ligand. With few exceptions,[11] the $\{Ti(cat)_3\}$ polyhedra (cat = catecholato dianion) in such complexes adopt an octahedral coordination geometry. In contrast, $\{Mo(bdt)_3\}$ polyhedra (bdt = benzene-*o*-dithiolato dianion) can adopt a trigonal-prismatic ($Mo^{VI}$) or an octahedral ($Mo^{V}$) configuration, depending on the oxidation state of the metal center.[12]

The reaction of three equivalents of $H_4$-**1** with one equivalent each of $[TiO(acac)_2]$ and $[MoCl_4(CH_3CN)_2]$ in the presence of $Li_2CO_3$ and $Na_2CO_3$ gives a dark green solution (see the Supporting Information). The ESI(−) mass spectrum of the resulting compound shows only one characteristic signal at *m*/*z* 457, which was assigned to the H-$[TiMo(\mathbf{1})_3]^{3-}$ anion. We assume that the presence of two different donor groups in the ligand aids in the selective formation of the heterobimetallic complex over the homobimetallic complexes $[Ti_2(\mathbf{1})_3]^{4-}$ and $[Mo_2(\mathbf{1})_3]^{4-}$. Addition of four equivalents of (PNP)Cl to the methanol solution yields, after 12 h, a dark green precipitate that is only soluble in DMF. Slow diffusion of diethyl ether into the saturated DMF solution leads to dark green single crystals of the dinuclear complex $(PNP)_4[TiMo(\mathbf{1})_3]$ (**2a**). Compound **2a** was characterized by NMR spectroscopy and X-ray diffraction analysis.

The $^1$H NMR spectrum of **2a** showed only one set of signals for the ligand $\mathbf{1}^{4-}$ (Figure 1), as was expected for a complex with $C_3$ symmetry and parallel ligands. Assignment of the proton resonances was achieved by 2D NMR spectroscopy experiments. The aromatic protons of the catecholato and the benzene-*o*-dithiolato groups gave rise to one triplet ($H_c$: $\delta = 6.43$ ppm and $H_i$: $\delta = 6.85$ ppm) and two doublets of doublets ($H_d$, $H_b$: $\delta = 6.31$, 7.25 ppm and $H_j$, $H_h$: $\delta = 7.68$, 7.63 ppm) each. The resonances of the protons between $\delta = 7.98$ and 8.06 ppm have been assigned to the 1,4-phenylendiamido spacer.

The signals of the amide protons in **2a** are shifted downfield by approximately 1.4 ppm ($H_g$: $\delta = 11.90$ ppm; $H_a$: $\delta = 11.94$ ppm) compared to those of the free ligand $H_4$-**1** ($\delta = 10.51$ and 10.53 ppm). We take this as an indication of the formation of strong N−H···O and N−H···S hydrogen bonds between the amide protons and the O and S donor atoms in the *ortho* positions of the aromatic ring. Only N−H···O hydrogen bonds have been observed in homobimetallic titanium complexes with directional benzene-*o*-dithiolato/catecholato ligands.[7] Similar hydrogen bonds have been described repeatedly for helicates with dicatecholato ligands.[13] The formation of the $\{Mo^{IV}(bdt)_3\}$ polyhedron in **2a** allows for the first time the formation of N−H···S hydrogen bonds. In addition to the different electronic features, we attribute this phenomenon to the different geometric parameters in $\{Ti^{IV}(bdt)_3\}$ and $\{Mo^{IV}(bdt)_3\}$ polyhedra. The $\{Mo^{IV}(bdt)\}$ unit is nearly planar,[12c,14] while the $\{Ti^{IV}(bdt)\}$ unit is folded along the S···S-vector.[6,7,14,15] This folding prevents the formation of N−H···S hydrogen bonds in dinuclear triple-stranded titanium helicates (Scheme 1, type **C**).

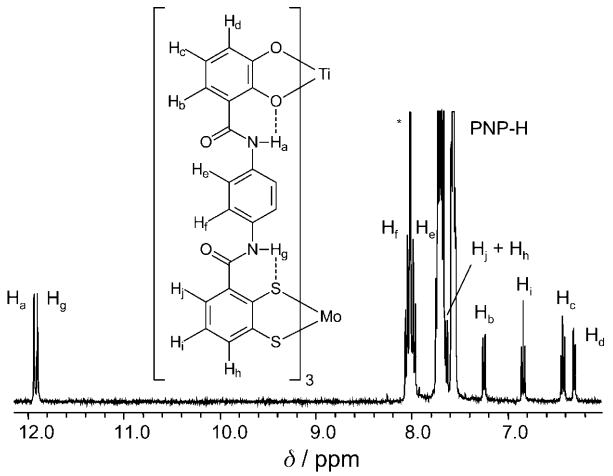


***Figure 1.*** $^1$H NMR spectrum in [D$_7$]DMF (*: DMF) of **2a**.

Crystals of $Li_{0.5}(PNP)_{3.5}[TiMo(\mathbf{1})_3]\cdot 4.5\,DMF\cdot 1.5\,EtOH\cdot H_2O$ (**2a**·4.5 DMF·1.5 EtOH·$H_2O$) were obtained by vapor diffusion of diethyl ether into a solution of $(PNP)_4[TiMo(\mathbf{1})_3]$ in DMF. The $(PNP)_4[TiMo(\mathbf{1})_3]$ used for crystallization experiments was found to contain some traces of lithium cations, which were not detected by NMR spectroscopy. The structure analysis (see the Supporting Information) revealed that the different binding preferences of the donor groups for the two metal ions lead to a parallel orientation of the ligand strands. The complex tetraanion $[TiMo(\mathbf{1})_3]^{4-}$ contains a distorted octahedral $\{Ti(cat)_3\}$ (twist angle $\varphi = 40.4°$) and a distorted trigonal-prismatic $\{Mo(bdt)_3\}$ polyhedron ($\varphi = 23.8°$; Figure 2).

The $\varphi$ values are typical for $[Ti(cat)_3]^{2-}$[16] and $[Mo^{IV}(bdt)_3]^{2-}$ complexes.[12c] The helical twist between the two Λ-configured metal centers ($d$(Mo···Ti) = 12.423(15) Å) in $[TiMo(\mathbf{1})_3]^{4-}$ measures 42.6°. Since the compound crystallizes in a centrosymmetric space group, the Δ,Δ-enantiomer is also present in the crystal lattice.

The Ti−O[7–9] and Mo−S bond lengths[12] fall in the range reported for similar complexes. As was concluded from the $^1$H NMR spectrum, the structure analysis reveals N−H···O ($d$(H···O) = 2.148 Å) and N−H···S hydrogen bonds ($d$(H···S) = 2.169 Å). In the solid state, two enantiomeric

  

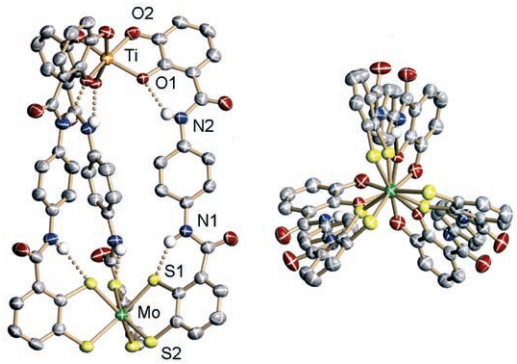


***Figure 2.*** Molecular structure of the tetraanion $[TiMo(\mathbf{1})_3]^{4-}$ of **2a** in side view (left) and along the Mo–Ti axis (right). Selected bond lengths [Å] and angles [°]: Ti–O1 2.017(3), Ti–O2 1.940(3), Mo–S1 2.381(1), Mo–S2 2.364(1), Ti···Mo 12.423(15); O1-Ti-O2 79.34(11), S1-Mo-S2 81.24(3), Ti-O-C 114.5(2)–116.6(2), Mo-S-C 110.22(14)–111.21(14).

helicates, Λ,Λ-$[TiMo(\mathbf{1})_3]^{4-}$ and Δ,Δ-$[TiMo(\mathbf{1})_3]^{4-}$, are connected though a PNP cation, which resides on a crystallographic inversion center. This arrangement leads to a tetranuclear unit $\{[TiMo(\mathbf{1})_3]\text{-}(PNP)\text{-}[TiMo(\mathbf{1})_3]\}^{7-}$ (Figure 3, left). The complete formula for this dimer is $\{(PNP)_3\text{-}[TiMo(\mathbf{1})_3]\text{-}(PNP)\text{-}[TiMo(\mathbf{1})_3](PNP)_3\}^{-}$. The lithium cation missing for charge neutrality could not be located by X-ray crystallography.

The importance of alkali metal cations for the stereoselective self-organization of dinuclear triple-stranded helicates has been described several times.[3,17] The aggregation of helicates of type $[TiMo(\mathbf{1})_3]^{4-}$ is also controlled by the nature and number of available alkali metal cations.

Addition of only two equivalents of (PNP)Cl to a methanolic solution containing the components $Ti^{IV}/Mo^{IV}/\mathbf{1}^{4-}$ in the stoichiometric ratio 1:1:3 and subsequent 12 h stirring does not lead to insoluble $(PNP)_4[TiMo(\mathbf{1})_3]$ (**2a**) but instead to $Li_{1.5}Na_{0.5}(PNP)_2[TiMo(\mathbf{1})_3]$ (**2b**), which is soluble in methanol (Scheme 2). This complex can be crystallized as black needles by vapor diffusion of diethyl ether into the methanolic solution. Crystals of composition $Li_{1.5}Na_{0.5}(PNP)_2\text{-}[TiMo(\mathbf{1})_3]\cdot 6H_2O$ (**2b**·$6H_2O$) were obtained in this manner. The X-ray diffraction analysis revealed that the compound crystallized in the acentric monoclinic space group *C*2. The geometric parameters of the anions $[TiMo(\mathbf{1})_3]^{4-}$ in **2a** and **2b** differ only marginally. The helical twist of 44.3° for **2b** and the twist angles ($\varphi = 35°$ {Ti(cat)$_3$}; $\varphi = 20.6°$ {Mo(bdt)$_3$}) are also nearly identical to the values observed for **2a**.

The aggregation of the helical anions of **2b** in the solid state is, however, determined by the nature of the cations. As described above, in **2a** a PNP cation residing on a crystallographic inversion center bridges two enantiomeric helicates through {Mo(bdt)$_3$}–PNP interactions, leading to $\{\Lambda,\Lambda\text{-}[TiMo(\mathbf{1})_3]\text{-}(PNP)\text{-}\Delta,\Delta\text{-}[TiMo(\mathbf{1})_3]\}^{7-}$ (Figure 3, left). In **2b**, however, two {Ti(cat)$_3$} polyhedra interact with a sodium cation, leading to dimers of type $\{\Delta,\Delta\text{-}[TiMo(\mathbf{1})_3]\text{-}Na\text{-}\Delta,\Delta\text{-}[TiMo(\mathbf{1})_3]\}^{7-}$, in which two homochiral helicates are connected by the sodium cation (Figure 3, right).

Furthermore, the $C_3$-symmetry is not preserved for the helical anion of **2b**. This effect is caused by lithium cations that are coordinated in a bridging fashion by carbonyl oxygen atoms of two different $[TiMo(\mathbf{1})_3]^{4-}$ anions. The interaction of the lithium and sodium cations leads to the formation of a polymeric network in the solid state (see the Supporting Information). One half cation equivalent (most likely 0.5 $Li^+$) is missing. Its positional parameters could not be determined by X-ray crystallography, most likely owing to disorder.

We have shown that the directional ligand $H_4$-**1** reacts with $Mo^{IV}$ and $Ti^{IV}$ to give heterobimetallic triple-stranded helicates with a parallel orientation of the ligand strands. The helical anions of type $[TiMo(\mathbf{1})_3]^{4-}$ are formed as a pair of racemic Λ,Λ and Δ,Δ stereoisomers. During crystallization in the presence of four equivalents of (PNP)Cl, the complex anion $\{\Lambda,\Lambda\text{-}[TiMo(\mathbf{1})_3]\text{-}(PNP)\text{-}\Delta,\Delta\text{-}[TiMo(\mathbf{1})_3]\}^{7-}$ was obtained. It coexists together with its enantiomer in a centrosymmetric crystal lattice. Crystallization in the presence of only two equivalents of (PNP)Cl leads to optical resolution and formation of the complex anion $\{\Delta,\Delta\text{-}[TiMo(\mathbf{1})_3]\text{-}Na\text{-}\Delta,\Delta\text{-}[TiMo(\mathbf{1})_3]\}^{7-}$, which crystallizes in an acentric space group. Crystals of the enantiomeric dimer exist in additional crystals. Strong N–H···O and N–H···S hydrogen bonds are observed for the first time in the $[TiMo(\mathbf{1})_3)]^{4-}$ anions. We attribute this to the planar geometry of the {Mo(bdt)} moiety,[12,14] while similar homodinuclear $Ti^{IV}$ helicates contain a {Ti(bdt)} unit which is severely bent about the S···S vector,[6,7,14,15,18] effectively preventing the formation of N–H···S hydrogen bonds. Future experiments are designed to reveal whether the $\{M^{IV}(bdt)_3\}$ polyhedra in helicates such as **2a** and **2b** can be oxidized to give trigonal-prismatic $Mo^{VI}$ species under loss of helicity of the dinuclear triple-stranded complex.

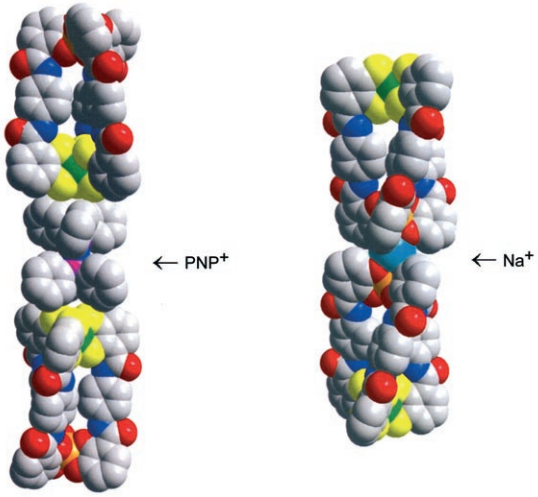


***Figure 3.*** Molecular structures of the supramolecular aggregates $\{\Lambda,\Lambda\text{-}[TiMo(\mathbf{1})_3]\text{-}(PNP)\text{-}\Delta,\Delta\text{-}[TiMo(\mathbf{1})_3]\}^{7-}$ (left) and $\{\Delta,\Delta\text{-}[TiMo(\mathbf{1})_3]\text{-}Na\text{-}\Delta,\Delta\text{-}[TiMo(\mathbf{1})_3]\}^{7-}$ (right). The color code is the same as in Figure 2.

Received: March 11, 2008
Revised: April 25, 2008
Published online: July 24, 2008

  

**Keywords:** helical structures · heterometallic complexes · O,S ligands · template synthesis


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