

Metallosupramolecular Chemistry with Bis(benzene-*o*-dithiolato) Ligands

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Abstract: The bis(benzene-*o*-dithiol) ligands H₄-1, H₄-2, and H₄-3 react with [Ti(OC₂H₅)₄] to give dinuclear triple-stranded helicates [Ti₂L₃]⁴⁻ (L = 1⁴⁻, 2⁴⁻, 3⁴⁻). NMR spectroscopic investigations revealed that the complex anions possess C₃ symmetry in solution. A crystal structure analysis for (PNP)₄[Ti₂(2)₃] ((PNP)₄[14]) confirmed the C₃ symmetry for the complex anion in the solid state. The complex anion in Li(PNP)₃[Ti₂(1)₃] (Li(PNP)₃[13]) does not exhibit C₃ symmetry in the solid state due to the formation of polymeric chains of lithium bridged complex anions. Complexes [13]⁴⁻ and [14]⁴⁻ were obtained as racemic mixtures of the Δ,Δ and Λ,Λ isomers. In contrast to that, complex (PNP)₄[Ti₂(3)₃] ((PNP)₄[15]) with the enantiomerically pure chiral ligand 3⁴⁻ shows a strong Cotton effect in the CD spectrum, indicating that the chirality of the ligands leads to the formation of chiral metal centers. The *o*-phenylene diamine bridged bis(benzene-*o*-dithiol) ligand H₄-4 reacts with Ti⁴⁺ to give the dinuclear double-stranded complex Li₂[Ti₂(4)₂(μ-OCH₃)₂] containing two bridging methoxy ligands between the metal centers. The crystal structure analysis and the ¹H NMR spectrum of (Ph₄As)₂[Ti₂(4)₂(μ-OCH₃)₂] ((Ph₄As)₂[16]) reveal C₂ symmetry for the anion [Ti₂(4)₂(μ-OCH₃)₂]²⁻. For a comparative study the dicatchol ligand H₄-5, containing the same *o*-phenylene diamine bridging group as the bis(benzene-*o*-dithiol) ligands H₄-4, was prepared and reacted with [TiO(acac)₂] to give the dinuclear complex anion [Ti₂(5)₂(μ-OCH₃)₂]²⁻. The molecular structure of (PNP)₂[Ti₂(5)₂(μ-OCH₃)₂] ((PNP)₂[17]) contains a complex anion which is similar to [16]²⁻, with the exception that strong N–H⋯O hydrogen bonds are formed in complex anion [17]²⁻, while N–H⋯S hydrogen bonds are absent in complex anion [16]²⁻.

Introduction

The metal directed self-assembly of supramolecular coordination compounds has attracted much interest during the past two decades.¹ Several different structural motifs have been prepared in transition metal directed self-assembly reactions.² Among those, metallohelicates have attracted special interest owing to their presence in nature.³ Raymond et al. isolated the first triple-stranded helicate [Fe₂(RA)₃] (H₂RA = rhodothorulic acid) that contains exclusively oxygen donors from hydroxamate groups.⁴

The first metallohelicate analyzed by X-ray diffraction was described by Lehn et al. in 1987.⁵ It consists of two tris-

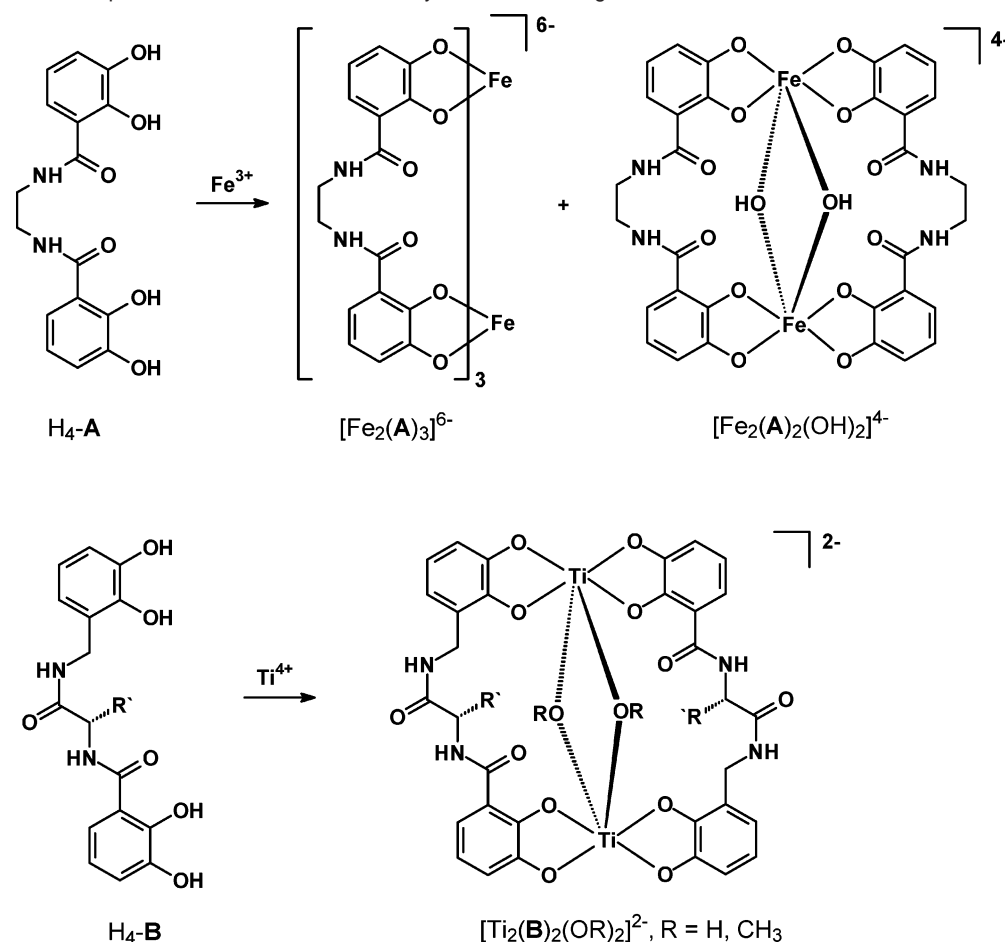
(bipyridine) ligands and three Cu(I) ions. During the following decade, the helicate chemistry was dominated by ligands with nitrogen donors such as oligopyrimidines. Later, Raymond,⁶ Stack,⁷ and Albrecht⁸ prepared a series of dicatchol ligands with different bridging groups that have been used for the preparation of dinuclear triple-stranded helicates.

Similar ligands with sulfur donors, e.g., with benzene-*o*-dithiolate donor groups, remained rare in supramolecular chemistry most likely owing to the difficulties encountered during the preparation of bis(benzene-*o*-dithiol) ligands. In 1995 we described a method for the *ortho*-functionalization of

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Scheme 1. Double- and Triple-Stranded Helicates Formed by Dicatecholato Ligands

benzene-1,2-dithiol that led to the preparation of the first bis(benzene-*o*-dithiol) ligands.⁹ Some dinuclear, nonhelical nickel complexes¹⁰ and a tetranuclear metallacycle¹¹ have been described with this type of ligand. A triple-stranded helicate with a directional benzene-*o*-dithiolato/catecholato ligand has also been described.¹²

Besides triple-stranded helicates, two other structural motifs have been obtained with dicatechol ligands. Depending on the topology of the ligands, tetrahedral M₄L₆ clusters¹³ or dinuclear double-stranded complexes^{7a,14} can be formed. Stack et al. reported the dicatechol ligand H₄-A (Scheme 1) that forms a triple-stranded helicate [Fe₂(A)₃]⁶⁻ or a dinuclear double-

stranded complex [Fe₂(A)₂(OH)₂]⁴⁻, depending on the metal/ligand ratio used for the complex preparation.^{7a} Albrecht et al. prepared a series of amino acid bridged dicatechol ligands H₄-B that exclusively form dinuclear double-stranded complexes [Ti₂(B)₂(OR)₂]²⁻ (R = CH₃, H) with the two coligands OR⁻ bridging the titanium atoms. With ligands of type B⁴⁻ no triple-stranded helicates have been obtained.¹⁴

We present here the synthesis and coordination chemistry of a series of bis(benzene-*o*-dithiol) ligands that are able to form either dinuclear triple-stranded helicates or double-stranded helical complexes with titanium(IV) ions, depending on the ligand backbone. The ligands H₄-1 and H₄-2 (Figure 1) form racemic mixtures of dinuclear triple-stranded helicates, while the enantiomerically pure ligand H₄-3 leads to a chirality transfer to the metal centers in a triple-stranded helicate. A dinuclear double-stranded complex is obtained with ligand H₄-4 and Ti^{IV}. For a comparison of dicatechol and bis(benzene-*o*-dithiol) ligands we prepared the dicatechol ligand H₄-5, which exhibits the same topology as H₄-4, and studied its coordination chemistry with Ti^{IV}. A preliminary report on the coordination chemistry of H₄-1 has already appeared.¹⁵

Results and Discussion

Ligand Synthesis. The synthesis of the ligands H₄-1, H₄-2, H₄-3, and H₄-4 is depicted in Scheme 2 and was carried out according to previously reported methods.¹⁰ 2,3-Di(isopropyl-

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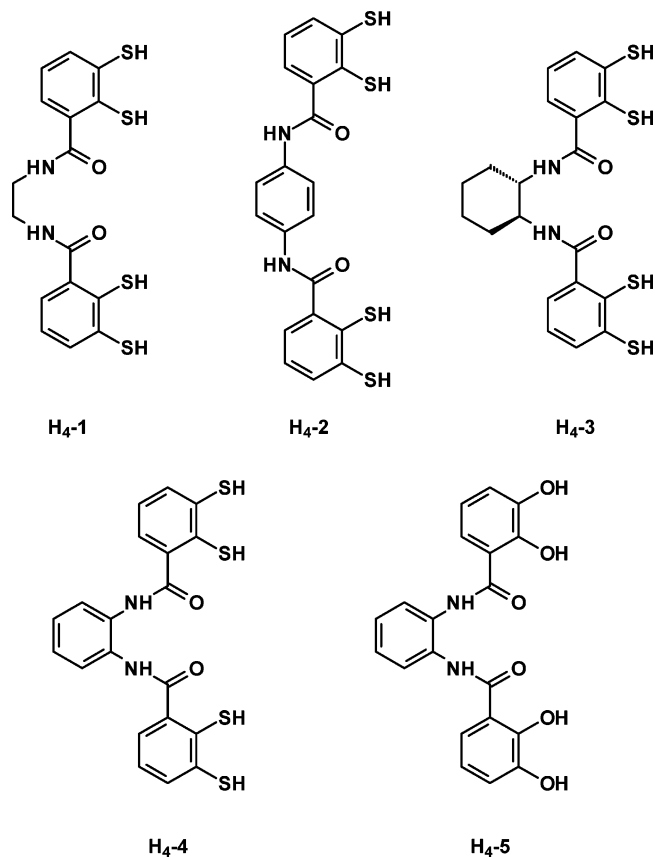


Figure 1. Ligands investigated in this study.

mercapto) benzoic acid **6** was prepared as we have described earlier.^{9,10} Treatment of **6** with oxalyl dichloride in benzene yields within 60 min the acid chloride **7**. The bridging of two molecules of **7** with different diamines in the presence of triethylamine affords the *S*-alkylated compounds **8–11** in yields of 80–95%. The protection groups at the sulfur atoms were removed by treatment of **8–11** with sodium/naphthalene followed by acid hydrolysis. Ligands H₄-1–H₄-4 were obtained as off-white powders.

The dicatchol ligand H₄-5 was prepared according to a method developed by Raymond et al. (Scheme 3).^{6c,13b} 1,2-Dimethoxybenzoic acid chloride (2 equiv) was reacted with 1,2-phenylenediamine (1 equiv) to form the *O*-methylated compound **12**. The methyl protection groups were removed with BBr₃ followed by hydrolysis to afford H₄-5 in 90% yield as a white solid.

Preparation of Triple-Stranded Helicates. The formation of dinuclear titanium complexes with bis(benzene-*o*-dithiolato) ligands requires the use of reactive metal precursors such as [Ti(OC₂H₅)₄]. Less reactive compounds such as [TiO(acac)₂], which have been used successfully by Albrecht et al. for the preparation of dinuclear complexes with dicatcholato ligands,^{8,14} do not lead to defined products. Treatment of 3 equiv of the ligands H₄-1, H₄-2, or H₄-3 with 2 equiv of [Ti(OC₂H₅)₄] in methanol in the presence of Li₂CO₃ under an argon atmosphere yields deep red solutions that contain the compounds Li₄[Ti₂(L)₃] (L = 1⁴⁻, 2⁴⁻, 3⁴⁻) (Scheme 4). In the presence of Na₂CO₃ and K₂CO₃ instead of Li₂CO₃, the corresponding complexes Na₄[Ti₂(L)₃] and K₄[Ti₂(L)₃] are formed, indicating that the type of alkali metal cation does not have an influence on the composition of the assembled complex anion. However, the

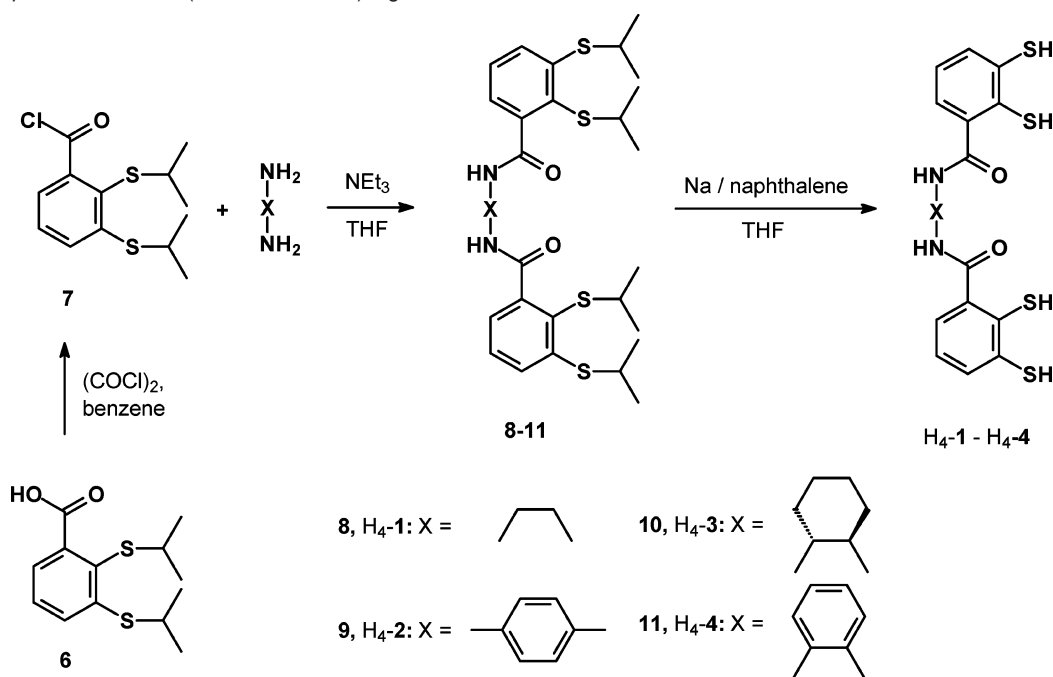
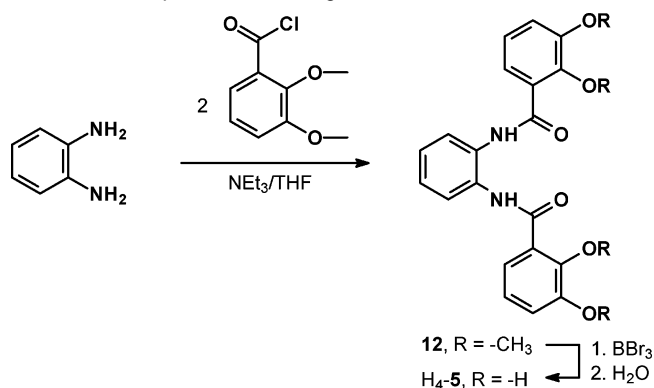
complexes M₄[Ti₂(1)₃], M₄[Ti₂(2)₃], and M₄[Ti₂(3)₃] (M = Li⁺, Na⁺, K⁺) could not be isolated in analytically pure form. The alkali metal cations were therefore exchanged for large organic cations. Addition of 4 equiv of (PNP)Cl (PNP⁺ = bis(triphenylphosphoranylidene)ammonium) or (Ph₄As)Cl, respectively, to the methanol solutions of Li₄[Ti₂(2)₃] and Li₄[Ti₂(3)₃] leads to the precipitation of the red-brown solids (PNP)₄[Ti₂(2)₃] ((PNP)₄-[**14**]) and (Ph₄As)₄[Ti₂(3)₃] ((Ph₄As)₄[**15**]). These salts are only soluble in DMF. In contrast to this, the addition of 4 equiv of (PNP)Cl to a solution of Li₄[Ti₂(1)₃] in methanol yields Li(PNP)₃[Ti₂(1)₃] (Li(PNP)₃[**13**]) as a brown precipitate. We have not been able to exchange the fourth lithium cation in Li(PNP)₃-[**13**], even when using a large excess of (PNP)Cl (10 equiv).

The use of the larger cations allowed the isolation of the salts Li(PNP)₃[**13**], (PNP)₄[**14**], and (Ph₄As)₄[**15**] in analytically pure form after recrystallization from DMF/diethyl ether in 60–80% yield. The composition of the salts was established by elemental analysis and ESI mass spectroscopy. Characteristic peaks with correct isotopic patterns were detected for Li(PNP)₃[Ti₂(1)₃] at *m/z* = 424 [M – 3PNP – Li + H]³⁻ and 604 [M – 2PNP – Li]³⁻, for (PNP)₄[Ti₂(2)₃] at *m/z* = 652 [M – 3PNP]³⁻ and 1247 [M – 2PNP]²⁻, and for (Ph₄As)₄[Ti₂(3)₃] at *m/z* = 478 [M – 4Ph₄As + H]³⁻ and 606 [M – 3Ph₄As]³⁻.

¹H NMR Studies. The triple-stranded helical anions [**13**]⁴⁻, [**14**]⁴⁻, and [**15**]⁴⁻ show very simple ¹H NMR spectra with only one set of signals for the protons for the three ligand strands, indicating C₃ symmetry for the complex anions in solution. For each complex, the signals for the aromatic protons of the benzene-*o*-dithiolato units appear as two doublets and a triplet, typical for an AMX spin system.

The signals for the protons attached to the benzene-*o*-dithiolato groups in complexes [**14**]⁴⁻ and [**15**]⁴⁻ are shifted highfield compared to the free ligands H₄-2 and H₄-3 (range Δδ = –0.54 to –0.25 ppm). We assume that the observed highfield shift is due to the quadruple negative charge of the helical anions. The resonances for the protons of the benzene-*o*-dithiolato units in [**13**]⁴⁻ are shifted downfield (range Δδ = 0.29 to 0.51 ppm) relative to H₄-1. This observation can be attributed to the formation of a cation–anion pair Li⁺[**13**]⁴⁻ with a reduced overall negative charge. Precisely this type of interaction occurs in the solid state and was observed in the crystal structure of Li(PNP)₃[Ti₂(1)₃] (Figure 4, *vide infra*). The exact binding site of the lithium cation at [**13**]⁴⁻ in solution remains unknown. However, it is reasonable to assume that the lithium cation is coordinated by carbonyl functions of the ligands in a fashion similar to that found in the crystal structure (Figure 4). However, the three ligand strands 1⁴⁻ in one anion [Ti₂(1)₃]⁴⁻ cannot coordinate simultaneously to one lithium cation. This geometric limitation should actually rule out the observed C₃ symmetry in solution. We believe that a fast exchange of the lithium cation between the carbonyl functions of the ligand strands and probably the solvent (DMF) occurs in solution. ¹H NMR investigations at –60 °C did not lead to the observation of more than one set of signals which in turn corroborates the assumption of a labile coordinated lithium cation.

We have recently shown that ¹H NMR spectroscopy is a powerful method to detect N–H⋯S hydrogen bonds in complexes with amide substituted benzene-*o*-dithiolato ligands.¹⁵ The signals for the amide protons in the complex anions [**13**]⁴⁻

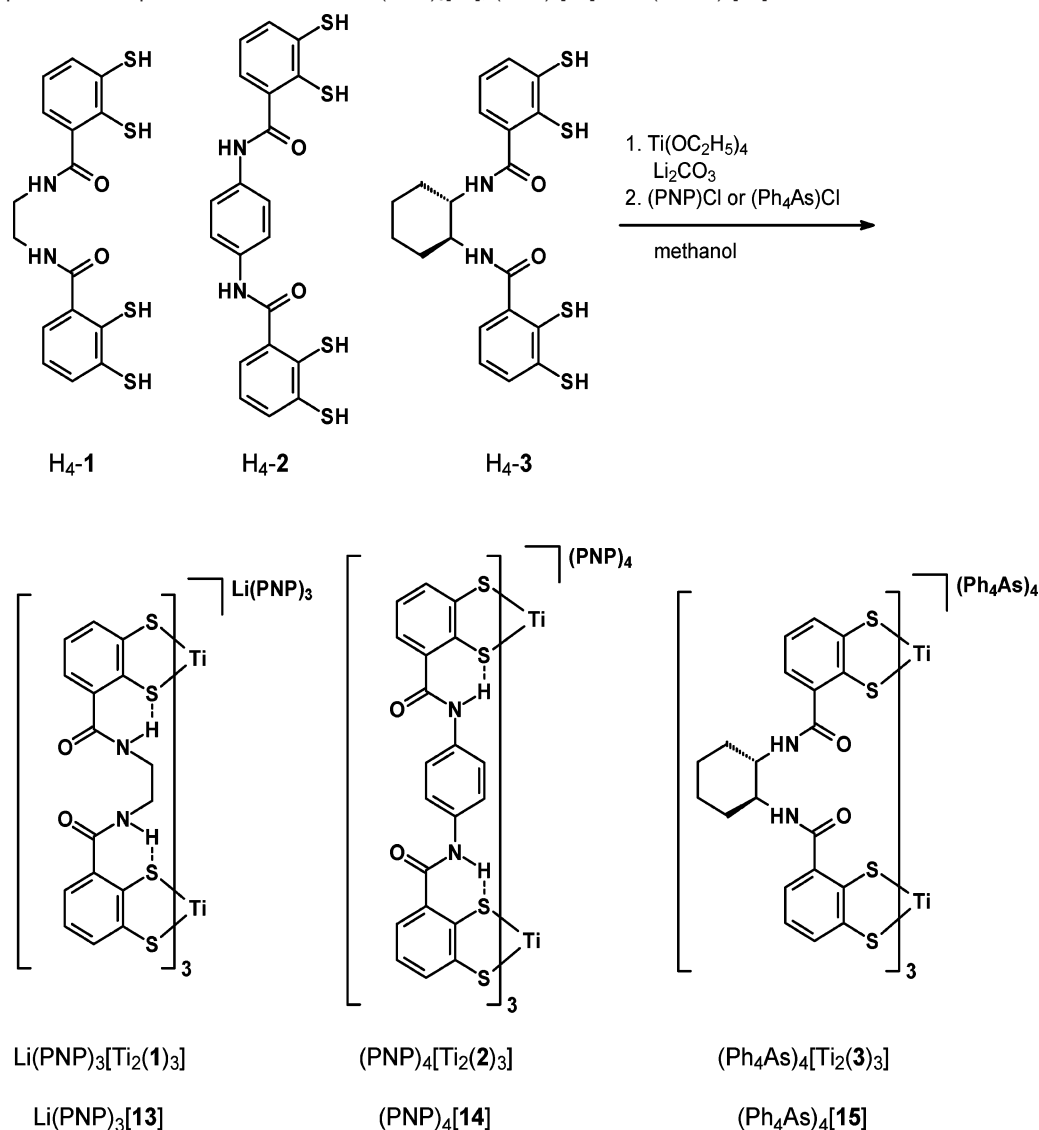
Scheme 2. Preparation of the Bis(benzene-*o*-dithiol) Ligands**Scheme 3.** Preparation of the Ligand H₄-5

and [14]⁴⁻ are shifted downfield relative to H₄-1 ($\Delta\delta = 0.85$ ppm) and H₄-2 ($\Delta\delta = 0.53$ ppm), respectively. This indicates the presence of strong N–H \cdots S hydrogen bonds in a six-membered ring between the amide protons and the *o*-thiolato atoms. So far, similarly strong N–H \cdots S hydrogen bonds have only been observed in more stable five-membered rings,¹⁶ while N–H \cdots O hydrogen bonds in six-membered rings are common in catechoylamido complexes¹² where they can have a structure determining influence.¹⁷

In contrast to the signals observed for the amide proton in [13]⁴⁻ and [14]⁴⁻, the signal for the amide protons in complex anion [15]⁴⁻ is shifted only slightly downfield relative to the free ligand H₄-3 ($\Delta\delta = 0.17$ ppm). Since the absence of N–H \cdots S hydrogen bonds normally leads to a highfield shift of the signal for the amide proton (vide infra), another kind of interaction must be responsible for this observation. So far we were unable to determine the molecular structure of (Ph₄As)₄[15]. Therefore a DFT modeling study (BP86/SV(P)) was carried out for the [Ti₂(3)₃]⁴⁻ anion in order to gain information about the conformation and the hydrogen bonds possible within the three ligands strands. The calculated molecular structure of the helical anion [Ti₂(3)₃]⁴⁻ reveals that interligand C=O \cdots H–N hydrogen bonds (H \cdots O 2.011 Å) are most likely formed instead of intraligand N–H \cdots S hydrogen bonds (Figure 2). The observed slight downfield shift for the amide protons in [15]⁴⁻ can therefore be ascribed to these interligand C=O \cdots H–N hydrogen bonds. The formation of intraligand N–H \cdots S hydrogen bonds is effectively prevented by the bulky cyclohexyl rings which are arranged nearly perpendicular to the Ti–Ti axis. Within this conformation steric interactions between the cyclohexyl rings and the rest of the complex anion are minimized. The signal for the CH protons of the cyclohexyl rings is observed as a broad doublet at $\delta = 4.34$ ppm due to coupling with the enantiotopic protons of the adjacent methylene groups. Only unresolved multiplets are observed for the methylene protons of the cyclohexyl ring, which is typical for such chiral rings.

Crystal Structure Analyses. We recently communicated the crystal structure of Li(PNP)₃[13]·3DMF·H₂O.¹⁵ Single crystals of (PNP)₃[14]·3DMF suitable for an X-ray diffraction analysis have been obtained by slow diffusion of benzene or diethyl ether into a solution of (PNP)₄[14] in DMF. Compound (PNP)₄[14]·3DMF crystallizes such as Li(PNP)₃[13]·3DMF·H₂O as a racemic mixture of the Λ, Λ and Δ, Δ isomers in the centrosym-

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Scheme 4. Preparation of Triple-Stranded Helicates $\text{Li}(\text{PNP})_3[\mathbf{13}]$, $(\text{PNP})_4[\mathbf{14}]$, and $(\text{Ph}_4\text{As})_4[\mathbf{15}]$ 

metrical space group $R\bar{3}c$ ($Z = 12$). The titanium atoms reside on a crystallographic 3-fold axis.

The molecular structures of the anions $[\text{Ti}_2(\mathbf{1})_3]^{4-}$ (Δ, Δ isomer) and $[\text{Ti}_2(\mathbf{2})_3]^{4-}$ (Λ, Λ isomer) are depicted in Figure 3. They confirm the formation of dinuclear triple-stranded helicates. The titanium atoms in both complex anions are coordinated by six thiolato donors in a slightly distorted octahedral fashion. The $\text{Ti}\cdots\text{Ti}$ separation measures 10.704 Å in complex $[\text{Ti}_2(\mathbf{1})_3]^{4-}$ and 12.954 Å in complex $[\text{Ti}_2(\mathbf{2})_3]^{4-}$ (Table 1). The molecular structure of the anion $[\text{Ti}_2(\mathbf{2})_3]^{4-}$ resembles the one reported for the dinuclear triple-stranded helicate with the corresponding dicatecholato ligand reported by Raymond et al.^{6c}

Short nonbonding intraligand $\text{N}\cdots\text{S}$ distances between the amide nitrogen atoms and the *ortho*-sulfur atoms of the adjacent benzene-*o*-dithiolato groups are found in both helical anions ($\text{N}\cdots\text{S}$ nonbonding distances of 2.992–3.050 Å for $[\text{Ti}_2(\mathbf{1})_3]^{4-}$ and 3.008–3.029 Å for $[\text{Ti}_2(\mathbf{2})_3]^{4-}$). The benzene-*o*-dithiolato and the amide subunits are arranged in a nearly coplanar fashion (dihedral angles 0.89°–27.02° for $[\text{Ti}_2(\mathbf{1})_3]^{4-}$ and 24.84°–28.59° for $[\text{Ti}_2(\mathbf{2})_3]^{4-}$). This small dihedral angle supports the presence of strong $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds which are also indicated by the ^1H NMR spectra. As a consequence, the $\text{Ti}-\text{S}$

bond lengths to the sulfur atoms in *ortho*-position to the amide functions are elongated (2.4404(10)–2.4592(11) Å for $[\text{Ti}_2(\mathbf{1})_3]^{4-}$ and 2.4288(15)–2.4358(14) Å for $[\text{Ti}_2(\mathbf{2})_3]^{4-}$), while the $\text{Ti}-\text{S}$ bond lengths to the sulfur atoms in *meta*-position are shorter (2.3478(10)–2.3766(10) Å for $[\text{Ti}_2(\mathbf{1})_3]^{4-}$ and 2.3810(14)–2.3831(15) Å for $[\text{Ti}_2(\mathbf{2})_3]^{4-}$).

The lithium cation in crystals of compound $\text{Li}(\text{PNP})_3[\mathbf{13}] \cdot 3\text{DMF} \cdot \text{H}_2\text{O}$ is coordinated by two carbonyl groups of two different anions $[\mathbf{13}]^{4-}$ and by the water and one DMF molecule in the asymmetric unit. This leads to indefinite polymeric chains $\text{Li}-[\mathbf{13}]^{4-}-\text{Li}-[\mathbf{13}]^{4-}$ in the crystal lattice (Figure 4). In contrast to this, the $[\text{Ti}_2(\mathbf{2})_3]^{4-}$ anions in compound $(\text{PNP})_4[\mathbf{14}] \cdot 3\text{DMF}$ are well separated with no interactions between cations and anions. The helical twist angles¹⁸ in both complex anions differ significantly. The rigid ligand $\mathbf{2}^{4-}$ in complex anion $[\mathbf{14}]^{4-}$ leads to a twist angle of 60°, while the more flexible ligand $\mathbf{1}^{4-}$ in complex anion $[\mathbf{13}]^{4-}$ causes a comparatively small twist angle of only 12°.

CD Spectroscopic Investigation of $(\text{Ph}_4\text{As})_4[\text{Ti}_2(\mathbf{3})_3]$. The triple-stranded helicate $(\text{Ph}_4\text{As})_4[\text{Ti}_2(\mathbf{3})_3]$ ($(\text{Ph}_4\text{As})_4[\mathbf{15}]$), as-

(18) Kepert, D. L. *Inorganic Stereochemistry: Inorganic Chemistry Concept 6*; Springer-Verlag: Berlin, 1982.

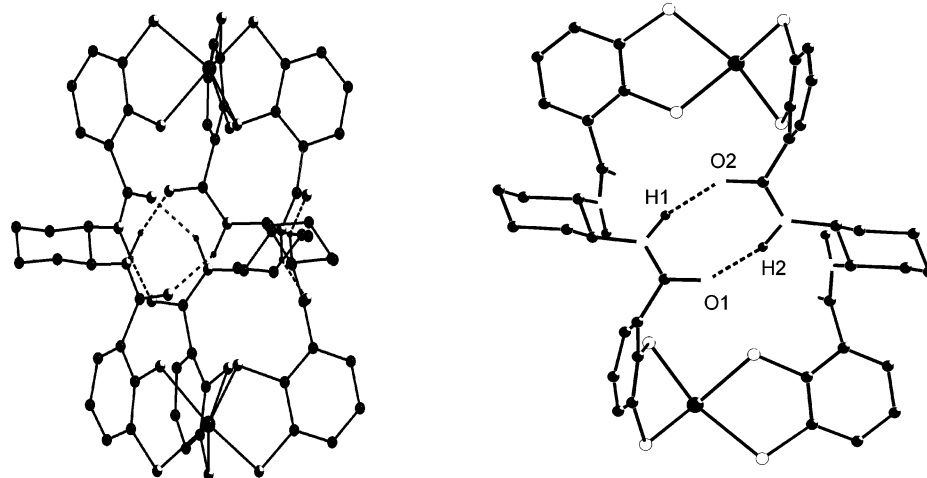


Figure 2. Calculated molecular structure of $[\text{Ti}_2(\mathbf{3})_3]^{4-}$ [$\mathbf{15}$] $^{4-}$ showing all six interligand $\text{C}=\text{O}\cdots\text{H}-\text{N}$ hydrogen bonds (left) and one selected pair of these hydrogen bonds (right). Only two of the three ligand strands are depicted in the picture on the right.

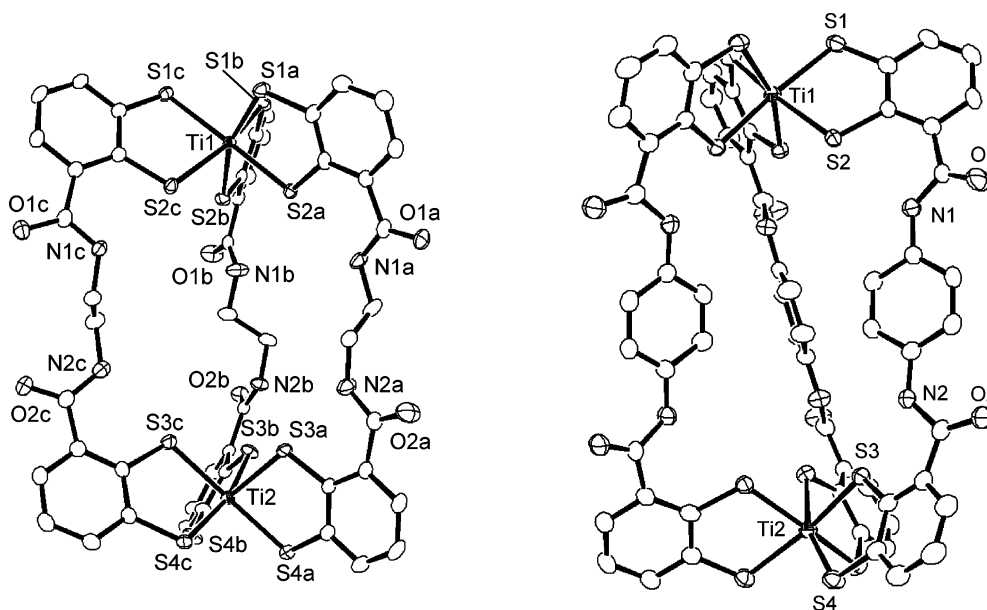


Figure 3. ORTEP diagrams of the anions $[\text{Ti}_2(\mathbf{1})_3]^{4-}$ and $[\text{Ti}_2(\mathbf{2})_3]^{4-}$. Hydrogen atoms have been omitted for clarity.

sembled from the chiral ligand $\text{H}_4\text{-4}$ and Ti^{IV} , has been investigated by a circular dichroism (CD) spectroscopy. The electronic spectrum of $(\text{Ph}_4\text{As})_4[\mathbf{15}]$ (Figure 5, left) exhibits three absorption bands at 335 ($\epsilon = 52,000 \text{ M}^{-1} \text{ cm}^{-1}$), 428 ($\epsilon = 23,500 \text{ M}^{-1} \text{ cm}^{-1}$) and 546 nm ($\epsilon = 15,500 \text{ M}^{-1} \text{ cm}^{-1}$). Similar absorptions have been reported for the related mononuclear complex $[\text{NH}_2(\text{CH}_3)_2]_2[\text{Ti}(\text{S}_2\text{C}_6\text{H}_4)_3]$.¹⁹ The corresponding transitions can be assigned to ligand-to-metal charge-transfer bands due to the large absorption coefficients. These absorptions are useful for the detection of chirality located at the metal center.

The CD spectrum of $(\text{Ph}_4\text{As})_4[\mathbf{15}]$ was measured between 300 and 700 nm, and it shows an intensive absorption with a positive Cotton effect at 546 nm ($\Delta\epsilon = 37.3 \text{ M}^{-1} \text{ cm}^{-1}$) and a less intensive absorption with a negative Cotton effect at 428 nm ($\Delta\epsilon = -27.8 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure 5, right). No Cotton effect was observed at 335 nm, the region with the most intensive absorption in the electronic spectrum. We assume that this absorption might be caused by a nonmetal-centered transition

or by a dipole forbidden transition. The large values for $\Delta\epsilon$ for the absorptions exhibiting a Cotton effect indicate that the chirality is transferred from the ligands to the titanium centers.

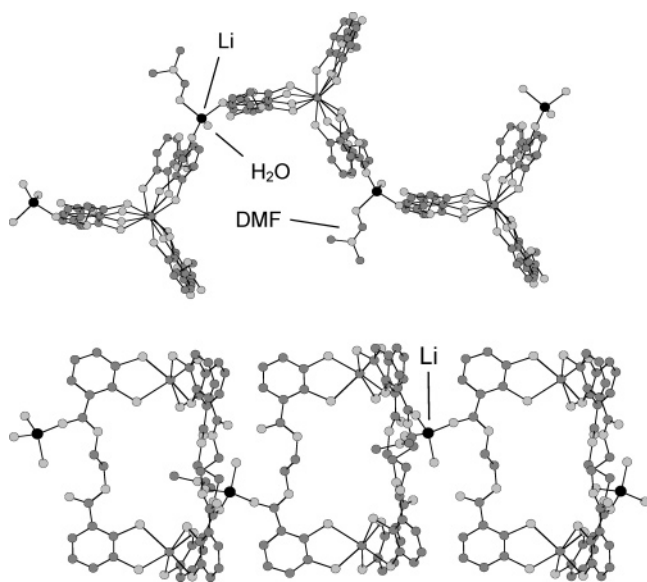
Preparation of Dinuclear Double-Stranded Bis(μ -methoxy) Bridged Complexes. The reaction of 1 equiv of $\text{H}_4\text{-4}$ with 1 equiv of $[\text{Ti}(\text{OC}_2\text{H}_5)_4]$ in the presence of Li_2CO_3 under an argon atmosphere in methanol yields a deep red solution of $\text{Li}_2[\text{Ti}_2(\mathbf{4})_2(\mu\text{-OCH}_3)_2]$ (Scheme 5, top). As was observed during the preparation of the triple-stranded helicates, an analytically pure compound $(\text{Ph}_4\text{As})_2[\text{Ti}_2(\mathbf{4})_2(\mu\text{-OCH}_3)_2]$ could be isolated by addition of $(\text{Ph}_4\text{As})\text{Cl}$. Addition of 2 equiv of $(\text{Ph}_4\text{As})\text{Cl}$ to the methanol solution of $\text{Li}_2[\text{Ti}_2(\mathbf{4})_2(\mu\text{-OCH}_3)_2]$ yields a brown precipitate of $(\text{Ph}_4\text{As})_2[\text{Ti}_2(\mathbf{4})_2(\mu\text{-OCH}_3)_2]$ ($(\text{Ph}_4\text{As})_2[\mathbf{16}]$) that is soluble in DMF and dimethyl sulfoxide. Negative ion ESI mass spectrometry of $(\text{Ph}_4\text{As})_2[\mathbf{16}]$ in acetonitrile reveals a characteristic signal at $m/z = 519$ for the $[\text{Ti}_2(\mathbf{4})_2(\mu\text{-OCH}_3)_2]^{2-}$ dianion with the correct isotope pattern.

Attempts to synthesize a dinuclear triple-stranded helicate $[\text{Ti}_2(\mathbf{4})_3]^{4-}$ from $\text{H}_4\text{-4}$ and Ti^{IV} failed. When the reaction among $\text{H}_4\text{-4}$, $[\text{Ti}(\text{OC}_2\text{H}_5)_4]$, and Li_2CO_3 is carried out with a metal-to-

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Table 1. Selected Bond Lengths (Å) and Angles (deg) in Complex Anions $[\text{Ti}_2(\mathbf{1})_3]^{4-}$ and $[\text{Ti}_2(\mathbf{2})_3]^{4-}$

| parameter | $\text{Li}(\text{PNP})_3[\text{Ti}_2(\mathbf{1})_3]$ | $(\text{PNP})_4[\text{Ti}_2(\mathbf{2})_3]$ |
|---------------------|--|---|
| Ti1–S1a(S1) | 2.3650(11) | 2.3810(15) |
| Ti1–S2a(S2) | 2.4503(10) | 2.4358(14) |
| Ti1–S1b | 2.3757(10) | |
| Ti1–S2b | 2.4520(11) | |
| Ti1–S1c | 2.3655(10) | |
| Ti1–S2c | 2.4478(10) | |
| Ti2–S3a(S3) | 2.4500(10) | 2.4288(15) |
| Ti2–S4a(S4) | 2.3766(10) | 2.3831(15) |
| Ti2–S3b | 2.4404(10) | |
| Ti2–S4b | 2.3665(11) | |
| Ti2–S3c | 2.4592(11) | |
| Ti2–S4c | 2.3478(10) | |
| Ti1...Ti2 | 10.704 | 12.954 |
| S1a(S1)–Ti1–S2a(S2) | 81.57(3) | 81.80(4) |
| S1b–Ti1–S2b | 82.27(3) | |
| S1c–Ti1–S2c | 80.83(3) | |
| S3a(S3)–Ti2–S4a(S4) | 81.27(3) | 81.83(4) |
| S3b–Ti2–S4b | 81.11(3) | |
| S3c–Ti2–S4c | 81.32(4) | |

**Figure 4.** Partial view of the polymeric chains in the crystal lattice of $\text{Li}(\text{PNP})_3[\mathbf{13}] \cdot 3\text{DMF} \cdot \text{H}_2\text{O}$.

ligand ratio of 2:3, only the double-stranded complex $\text{Li}_2[\text{Ti}_2(\mathbf{4})_2(\mu\text{-OCH}_3)_2]$ can be isolated. An increased reaction temperature of 60 °C also did not lead to the formation of a triple-stranded helicate. Upon heating of the reaction mixture, the color changes from red to yellow, indicating the decomposition of the initially formed double-stranded dinuclear complexes. The reaction of 1 equiv of $\text{Li}_2[\text{Ti}_2(\mathbf{4})_2(\mu\text{-OCH}_3)_2]$ or $(\text{Ph}_4\text{As})_2[\text{Ti}_2(\mathbf{4})_2(\mu\text{-OCH}_3)_2]$ with 1 equiv of ligand $\mathbf{4}^{4-}$ again leads only to the isolation of the double-stranded complex.

The coordination chemistry of the related dicatechol ligand $\mathbf{H}_4\text{-5}$ resembles the behavior observed for $\mathbf{H}_4\text{-4}$. Only the orange double-stranded complex $\text{Li}_2[\text{Ti}_2(\mathbf{5})_2(\mu\text{-OCH}_3)_2]$ is formed in the reaction of 1 equiv of $\mathbf{H}_4\text{-5}$ with 1 equiv of $[\text{TiO}(\text{acac})_2]$ (acac = acetylacetonato anion) and Li_2CO_3 in methanol under an argon atmosphere (Scheme 5, bottom). As was observed in the reaction of $\mathbf{H}_4\text{-4}$ with Ti^{IV} , no dinuclear triple-stranded helicate $[\text{Ti}_2(\mathbf{5})_3]^{4-}$ could be obtained from $\mathbf{H}_4\text{-5}$ and $[\text{TiO}(\text{acac})_2]$. Addition of 2 equiv of $(\text{PNP})\text{Cl}$ to the methanol solution of $\text{Li}_2[\text{Ti}_2(\mathbf{5})_2(\mu\text{-OCH}_3)_2]$ leads to the formation of $(\text{PNP})_2[\text{Ti}_2(\mathbf{5})_2(\mu\text{-OCH}_3)_2]$ ($(\text{PNP})_2[\mathbf{17}]$) as an orange precipitate.

The ESI mass spectrum of $(\text{PNP})_2[\mathbf{17}]$ reveals a characteristic peak at $m/z = 455$ for the $[\text{Ti}_2(\mathbf{5})_2(\mu\text{-OCH}_3)_2]^{2-}$ dianion with the correct isotope pattern.

^1H NMR Studies of $(\text{Ph}_4\text{As})_2[\mathbf{16}]$ and $(\text{PNP})_2[\mathbf{17}]$. Complex $[\mathbf{16}]^{2-}$ shows a simple ^1H NMR spectrum with only one set of signals which indicates C_2 symmetry of the complex anion in solution (Figure 6). Signals for the aromatic protons of the benzene-*o*-dithiolato groups are detected as a triplet at $\delta = 6.79$ ppm and two doublets of doublets at $\delta = 6.92$ and 7.11 ppm. The protons of the *o*-phenylenediamide spacer form an AA“XX”-spin system and two doublets of doublets are observed at $\delta = 7.15$ and 8.32 ppm. The singlet at $\delta = 4.60$ ppm belongs to the protons of the bridging methoxy group. The resonance for the amide protons appears as a singlet at $\delta = 9.77$ ppm. Compared to the free ligand $\mathbf{H}_4\text{-4}$, this resonance is shifted highfield ($\Delta\delta = -0.31$ ppm). The signals for the amide protons in complex anions $[\mathbf{13}]^{4-}$ and $[\mathbf{14}]^{4-}$, where intrastand N–H...S hydrogen bonds exist, are shifted downfield relative to the free ligands. We take the observation of the highfield shift for the amide protons in complex $[\text{Ti}_2(\mathbf{4})_2(\mu\text{-OCH}_3)_2]^{2-}$ as an indication that no N–H...S hydrogen bonds are formed in the complex anion in solution.

The ^1H NMR spectrum of $[\mathbf{17}]^{2-}$ also consists of only one set of signals and resembles the spectrum for complex anion $[\mathbf{16}]^{2-}$ except that the signal for the amide protons is shifted downfield compared to the free ligand $\mathbf{H}_4\text{-5}$ ($\Delta\delta = 0.28$ ppm). We take this as an indication for the expected formation of strong N–H...O hydrogen bonds in the anion $[\mathbf{17}]^{2-}$.

Molecular Structures of $[\mathbf{16}]^{2-}$ and $[\mathbf{17}]^{2-}$. Single crystals of $(\text{Ph}_4\text{As})_2[\text{Ti}_2(\mathbf{4})_2(\mu\text{-OCH}_3)_2] \cdot 4\text{DMF}$ which were suitable for an X-ray diffraction study have been obtained by slow vapor diffusion of diethyl ether into a solution of $(\text{Ph}_4\text{As})_2[\text{Ti}_2(\mathbf{4})_2(\mu\text{-OCH}_3)_2]$ in DMF within 2 weeks. The complex crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$. Figure 7 displays the molecular structure of the anion $[\text{Ti}_2(\mathbf{4})_2(\mu\text{-OCH}_3)_2]^{2-}$. The structure analysis confirms that a dinuclear double-stranded complex had formed. The two titanium atoms in $[\mathbf{16}]^{2-}$ are bridged by two ligand strands $\mathbf{4}^{4-}$ in addition to two methoxy groups, which form a central four-membered $[\text{Ti}(\mu\text{-OCH}_3)_2]$ ring. The coordination geometry at the metal centers is best described as strongly distorted octahedral with the oxygen atoms in a cis arrangement. The $\text{Ti}\cdots\text{Ti}^*$ separation of 3.1991(8) Å (Table 2) is characteristic for dinuclear titanium complexes with two μ -methoxy bridging groups and has been reported by Albrecht¹⁴ and Stack^{7a} for related complexes.

The complex anion $[\text{Ti}_2(\mathbf{4})_2(\mu\text{-OCH}_3)_2]^{2-}$ $[\mathbf{16}]^{2-}$ resides on a crystallographic inversion center. The two titanium atoms assume different configurations (Δ and Λ), which leads to the formation of a *meso* complex. As concluded from the ^1H NMR spectrum no N–H...S hydrogen bonds are observed in the solid state. The nonbonding N...S distances are relatively long (3.577 and 3.643 Å), compared to the helical complex anions $[\mathbf{13}]^{4-}$ (2.992–3.050 Å) and $[\mathbf{14}]^{4-}$ (3.008–3.029 Å) where strong N–H...S hydrogen bonds exist. In addition, the amide group and the benzene-*o*-dithiolato group are not coplanar in the anion $[\mathbf{16}]^{2-}$ (dihedral angles 95.47° and 89.69°) which also prevents the formation of N–H...S hydrogen bonds. The absence of N–H...S hydrogen bonds in $[\mathbf{16}]^{2-}$ leads to nearly uniform (2.4036(7)–2.4104(8) Å) Ti–S bond distances, which is in contrast to the triple-stranded helical anions $[\mathbf{13}]^{4-}$ and $[\mathbf{14}]^{4-}$,

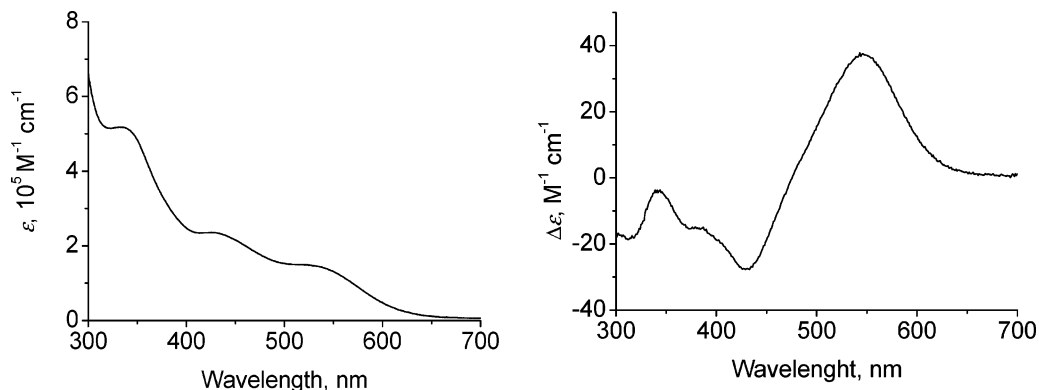
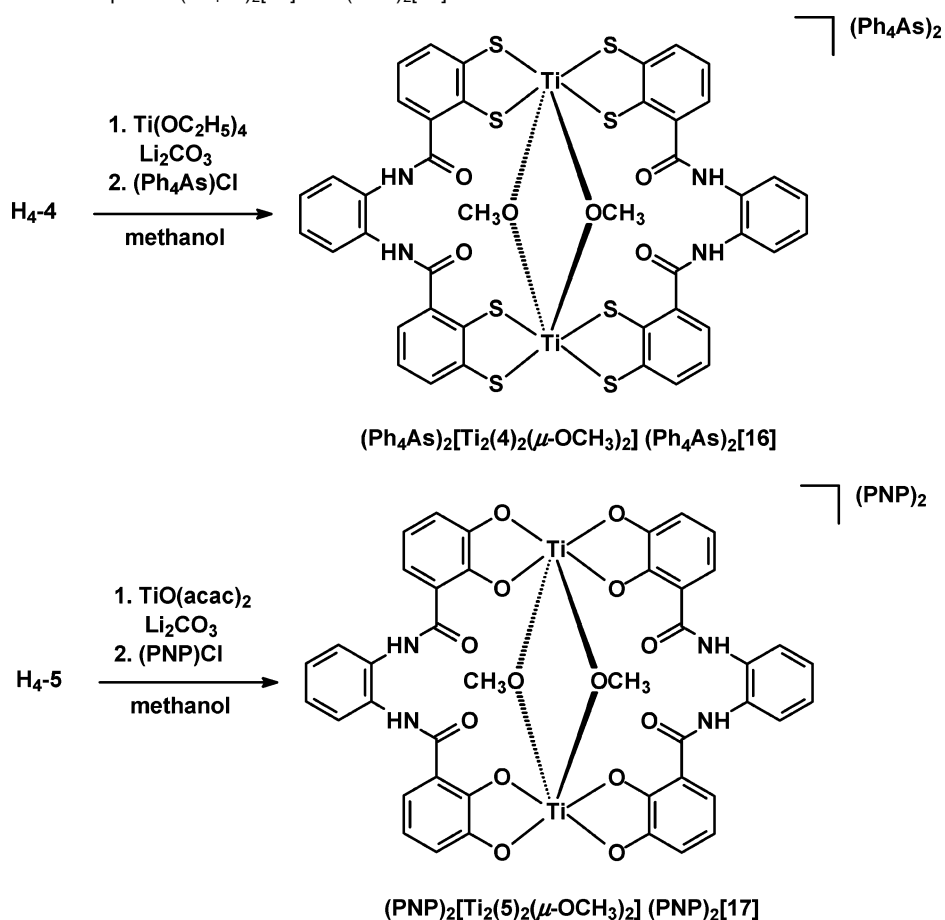


Figure 5. Electronic and CD spectra of $(\text{Ph}_4\text{As})_4[15]$, measured in DMF.

Scheme 5. Preparation of Complexes $(\text{Ph}_4\text{As})_2[16]$ and $(\text{PNP})_2[17]$



where the Ti–S distances to the thiolato donors involved in hydrogen bonding are longer than those not involved in N–H···S hydrogen bonds.

Single crystals of $(\text{PNP})_2[\text{Ti}_2(5)(\mu\text{-OCH}_3)_2] \cdot 2\text{CH}_3\text{CN} \cdot 2\text{CH}_3\text{-OH}$ have been grown by slow diffusion of diethyl ether into a solution of $(\text{PNP})_2[\text{Ti}_2(5)(\mu\text{-OCH}_3)_2]$ in acetonitrile/methanol (4:1). The complex crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$. The molecular structure of the anion $[\text{Ti}_2(5)(\mu\text{-OCH}_3)_2]^{2-}$ (Figure 8) resembles that of the anion $[\text{Ti}_2(4)(\mu\text{-OCH}_3)_2]^{2-}$. Again the complex anion resides on an inversion center, so that a *meso* complex with opposite configurations at the titanium atoms is formed. The Ti···Ti* distance (3.158 Å, Table 2) and the geometry of the $[\text{Ti}(\mu\text{-OCH}_3)_2]$ ring are comparable to the corresponding parameters in complex $[16]^{2-}$.

The nonbonding N···O_{ortho} distances (2.650(8)–2.721(8) Å) and the coplanarity of the catecholato ring and the amide function (dihedral angles 5.22° and 21.40°) reveal that the amide proton is engaged in a strong N–H···O hydrogen bond. This confirms the conclusions drawn from the ¹H NMR spectrum. Strong N–H···O hydrogen bonds have previously been observed in complexes obtained from amide bridged dicatecholato ligands.^{6c,7a,12,17} As a consequence of the strong N–H···O hydrogen bond, the Ti–O bond lengths within the catecholato group differ significantly.

The Ti–O bonds to the oxygen atoms in *ortho*-position to the amide group are elongated (1.959(5)–1.961(5) Å) while the Ti–O bonds to the oxygen atoms in *meta*-position are shorter (1.917(5)–1.921(5) Å). The comparison of the complex anions

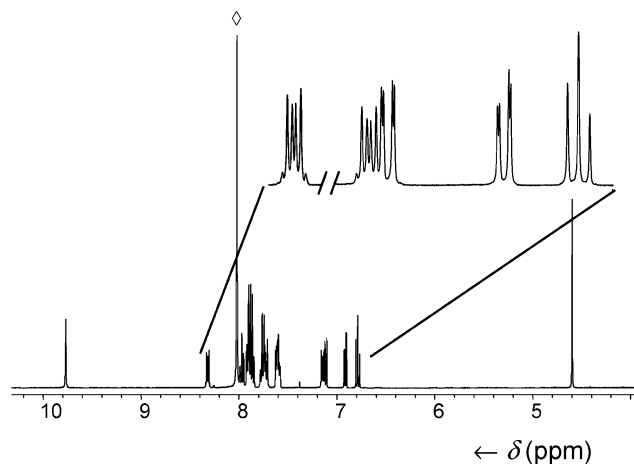


Figure 6. ^1H NMR spectrum of $(\text{Ph}_4\text{As})_2[16]$.

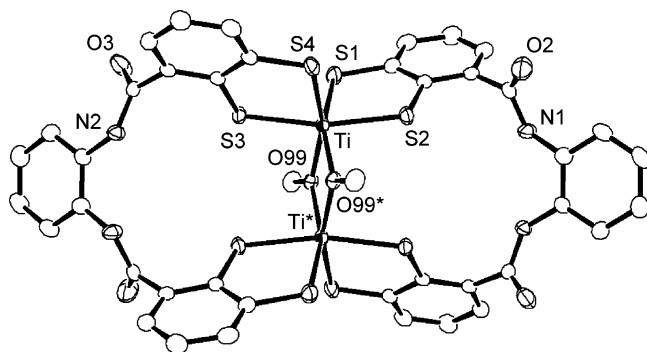


Figure 7. ORTEP diagram of the anion $[\text{Ti}_2(4)_2(\mu\text{-OCH}_3)_2]^{2-}$. Hydrogen atoms have been omitted.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in Complex Anions $[16]^{2-}$ and $[17]^{2-}$

| parameter | $[\text{Ti}_2(4)_2(\mu\text{-OCH}_3)_2]^{2-}$ | $[\text{Ti}_2(5)_2(\mu\text{-OCH}_3)_2]^{2-}$ |
|--------------------|---|---|
| Ti–S1(O1) | 2.4036(7) | 1.921(5) |
| Ti–S2(O2) | 2.4071(7) | 1.961(5) |
| Ti–S3(O3) | 2.4073(7) | 1.959(5) |
| Ti–S4(O4) | 2.4104(8) | 1.917(5) |
| Ti–O99 | 2.006(2) | 1.992(5) |
| Ti–O99* | 2.012(1) | 1.992(5) |
| N1···S2(O2) | 3.577 | 2.721 |
| N2···S3(O3) | 3.643 | 2.650 |
| S1(O1)–Ti–S2(O2) | 81.72(2) | 80.2(2) |
| S1(O1)–Ti–S3(O3*) | 89.13(3) | 92.0(2) |
| S1(O1)–Ti–S4(O4*) | 100.66(3) | 100.2(2) |
| S1(O1)–Ti–O99 | 95.11(5) | 159.5(2) |
| S1(O1)–Ti–O99* | 158.73(5) | 95.0(2) |
| S2(O2)–Ti–S3(O3*) | 167.07(3) | 168.8(2) |
| S2(O2)–Ti–S4(O4*) | 90.64(3) | 93.5(2) |
| S2(O2)–Ti–O99 | 106.57(5) | 84.9(2) |
| S2(O2)–Ti–O99* | 83.59(5) | 104.5(2) |
| S3(O3*)–Ti–S4(O4*) | 82.06(2) | 79.9(2) |
| S3(O3*)–Ti–O99 | 83.22(5) | 104.6(2) |
| S3(O3*)–Ti–O99* | 107.54(5) | 84.1(2) |
| S4(O4*)–Ti–O99 | 158.19(5) | 94.7(2) |
| S4(O4*)–Ti–O99* | 94.79(5) | 158.3(2) |
| O99–Ti1–O99* | 74.48(7) | 75.1(2) |
| Ti–O99–Ti* | 105.52(7) | 104.9(2) |

$[\text{Ti}_2(4)_2(\mu\text{-OCH}_3)_2]^{2-}$ and $[\text{Ti}_2(5)_2(\mu\text{-OCH}_3)_2]^{2-}$ demonstrated that the substitution of the oxygen atoms for sulfur atoms leads to identical structural motifs but different ligand conformations.

Conclusion

With this contribution we have shown that bis(benzene-*o*-dithiolato) ligands form triple- and double-stranded helicates

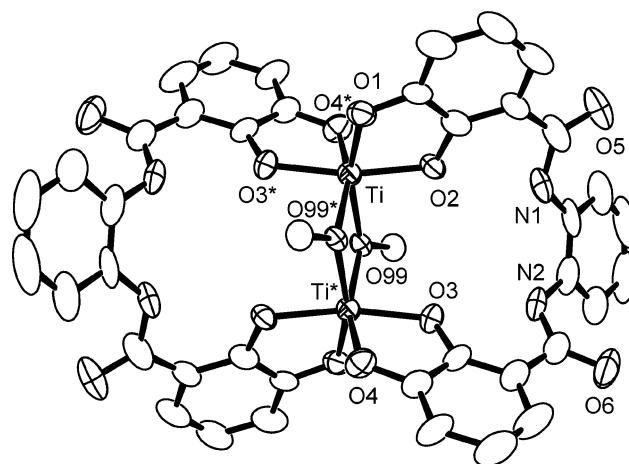


Figure 8. ORTEP diagram of the anion $[\text{Ti}_2(5)_2(\mu\text{-OCH}_3)_2]^{2-}$. Hydrogen atoms have been omitted.

with Ti^{IV} similar to those described for dicatecholato ligands. The type of bridging group between the benzene-*o*-dithiolato donor groups is responsible for the formation or absence of $\text{N}\cdots\text{H}\cdots\text{S}$ hydrogen bonds. The bridging group also determines the composition of the reaction product, e.g., the formation of triple- or double-stranded complexes.

It has been shown that benzene-*o*-dithiolato complexes of type $[\text{M}(\text{bdt})_3]^{n-}$ (bdt = benzene-*o*-dithiolato anion, $\text{M} = \text{W}$,²⁰ $n = 0, 1, 2$ and $\text{M} = \text{Mo}$,²¹ $n = 0, 1, 2$) can adopt a trigonal-prismatic (W^{VI} and Mo^{VI}) or octahedral (W^{V} and Mo^{V}) coordination geometry. Incorporation of these metals into triple-stranded dinuclear complexes with benzene-*o*-dithiolate ligands could lead to helicates (two octahedral metal centers) or nonhelical complexes (two trigonal-prismatic metal centers). Redox reactions could be used to interconvert the nonhelical complexes (two M^{VS}_6 polyhedra) into helical (two M^{IVS}_6 polyhedra), which in principle would allow switching on and off the helicity of a dinuclear triple-stranded complex with a bis(benzene-*o*-dithiolato) ligand. We are currently studying the preparation and properties of triple-stranded dinuclear tungsten and molybdenum complexes with bis(benzene-*o*-dithiolato) ligands.

Experimental Section

General. All operations were carried out under an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and freshly distilled prior to use. NMR spectra were recorded on Bruker AC 200 (200 MHz), Bruker AMX 400 (400 MHz), or Varian Inova 500 (500 MHz) and are reported relative to TMS as an internal standard or relative to the solvent signal. IR spectra were recorded on a Bruker Vector 22 infrared spectrometer. Mass spectra were measured on a Varian MAT 212 (EI), on a Micromass Quattro LC-Z (ESI), and on a Bruker Reflex IV spectrometer (MALDI). Elemental analyses were performed with a Vario EL III CHNS Elemental Analyzer. The electronic spectrum was recorded on a Varian Cary 50. 2,3-Di(isopropylmercapto)benzoic acid (**6**),^{9b} 1,2-bis(2,3-di(isopropylmercapto)benzamido)ethane **8**,¹⁰ 1,2-bis(2,3-dimercaptobenzamido)ethane **H₄-1**,¹⁰ and $\text{Li}(\text{PNP})_3[\text{Ti}_2(1)_3]$ $\text{Li}(\text{PNP})_3[13]$ ¹⁵ have been prepared as previously described.

1,2-Bis(2,3-di(isopropylmercapto)benzamido)ethane **8.**¹⁰ ^1H NMR (200 MHz, $[\text{d}_6]\text{DMSO}$): δ = 8.21 (s, br, 2H, CONH), 7.36 (d, 4H,

(20) Huynh, H. V.; Lügger, T.; Hahn, F. E. *Eur. J. Inorg. Chem.* **2002**, 3007–3009.

(21) Schulze Isfort, C.; Pape, T.; Hahn, F. E. *Eur. J. Inorg. Chem.* **2005**, 2607–2611.

ArH), 7.10 (t, 2H, ArH), 3.60 (m, $^3J_{\text{H,H}} = 6.3$ Hz, 2H, SCH), 3.38 (m, $^3J_{\text{H,H}} = 6.5$ Hz, 2H, SCH), 3.34 (s, 4H, CH₂), 1.30 (d, $^3J_{\text{H,H}} = 6.5$ Hz, 12H, CH(CH₃)₂), 1.11 ppm (d, $^3J_{\text{H,H}} = 6.3$ Hz, 12H, CH(CH₃)₂). ¹³C NMR (50 MHz, [d₆]DMSO): $\delta = 168.2$ (CONH), 145.5, 144.6, 128.8, 127.8, 126.4, 123.2 (ArC), 34.7 (CH(CH₃)₂), 22.9 (CH(CH₃)₂), 22.3 ppm (CH(CH₃)₂); one of the (CH(CH₃)₂) signals and the CH₂ signal of the bridge are obscured by the solvent peaks. MS (70 eV, EI): *m/z* (%) = 564 (46, M⁺), 521 (100, M⁺-C₃H₇), 253 (21), 211 (29), 43 (3, C₃H₇⁺). IR (KBr): $\tilde{\nu} = 3355, 3257$ (st, N-H), 2960, 2923, 2863 (m, SC-H), 1677 (st, C=O), 1550 (st, N-H), 1638, 1571, 1519 (m, Ar-C=C), 1442 cm⁻¹ (m, CH₂). Anal. Calcd for C₂₈H₄₀N₂O₂S₄: C, 59.54; H, 7.14; N, 4.96; S, 22.70. Found: C, 59.35; H, 7.00; N, 4.81; S, 22.73.

1,4-Bis(2,3-di(isopropylmercapto)benzamido)benzene (9). 2,3-Di(isopropylmercapto)benzoic acid **6** (3.82 g, 14.15 mmol) and DMF (2 drops) were dissolved in benzene (20 mL) and cooled to 5 °C. Oxalyl dichloride (1.85 mL, 21.23 mmol) was added, and the solution was stirred for 1 h at 5 °C. The solvent was removed in vacuo. The residue was dissolved in THF (20 mL) and added to a solution of 1,4-diaminobenzene (725 mg, 6.72 mmol) and NEt₃ (2.0 mL, 14.15 mmol) in THF (40 mL). The suspension obtained was stirred for 12 h at ambient temperature. NEt₃·HCl was filtered off, and the solvent was removed in vacuo. The resulting solid was washed with water and diethyl ether to give an off-white powder (3.38 g, 82%). ¹H NMR (200 MHz, CDCl₃): $\delta = 10.24$ (s, 2H, CONH), 7.65 (s, 4H, ArH), 7.44 (m, 4H, ArH), 7.21 (m, 2H, ArH), 3.65 (m, 2H, SCH), 3.44 (m, 2H, SCH), 1.33 (d, $^3J_{\text{H,H}} = 6.4$ Hz, 12H, CH(CH₃)₂), 1.13 ppm (d, $^3J_{\text{H,H}} = 6.4$ Hz, 12H, CH(CH₃)₂). ¹³C NMR (50 MHz, CDCl₃): $\delta = 166.5$ (CONH), 145.4, 144.8, 134.9, 129.2, 127.8, 126.4, 123.2, 119.8 (ArC), 36.2 (CH(CH₃)₂), 34.7 (CH(CH₃)₂), 23.0 (CH(CH₃)₂), 22.4 ppm (CH(CH₃)₂). MS (70 eV, EI): *m/z* (%) = 612 (100, M⁺), 360 (28), 270 (20), 211 (46), 108 (89), 41 (28). IR (KBr): $\tilde{\nu} = 3307$ (st, N-H), 3051 (s, Ar-H), 2960, 2923, 2863 (m, SC-H), 1665 (st, C=O), 1607, 1514 cm⁻¹ (m, Ar-C=C). Anal. Calcd for C₃₂H₄₀N₂O₂S₄: C, 62.71; H, 6.58; N, 4.57; S, 20.92. Found: C, 62.29; H, 6.43; N, 4.44; S, 20.88.

1,2-(*R,R*)-Bis(2,3-di(isopropylmercapto)benzamido)cyclohexane (10). Compound **10** was prepared as described for **9**. Yield 1.57 g (2.54 mmol, 78%) of a bright yellow powder. ¹H NMR (200 MHz, CDCl₃): $\delta = 7.29$ –7.19 (m, 6H, ArH), 6.87 (d, br, 2H, CONH), 3.94 (s, br, 2H, NCH), 3.53–3.39 (m, 4H, SCH), 2.28 (s, br, 2H, CH₂), 1.83 (s, br, 2H, CH₂), 1.38 (dd, 12H, CH₃), 1.22 (m, 4H, CH₂), 1.19 ppm (t, 12H, CH₃). ¹³C NMR (50 MHz, CDCl₃): $\delta = 169.0$ (CONH), 145.7, 143.2, 129.2, 128.8, 127.8, 124.6 (ArC), 54.0 (NCH), 40.2 (SCH), 36.0 (SCH), 32.2 (CH₂), 24.7 (CH₂), 23.2 (CH₃), 22.9 (CH₃), 22.6 ppm (CH₃). MS (MALDI): *m/z* = 619 [M⁺]. IR (KBr): $\tilde{\nu} = 3285$ (st, N-H), 2960, 2926, 2861 (m, SC-H), 1639 (st, C=O), 1529 (m, N-H), 795 cm⁻¹ (m, Ar-H). Anal. Calcd for C₃₂H₄₆N₂O₂S₄: C, 62.10; H, 7.49; N, 4.53; S, 20.72. Found: C, 61.65; H, 8.01; N, 4.58; S, 20.56.

1,2-Bis(2,3-di(isopropylmercapto)benzamido)benzene (11). Compound **11** was prepared as described for **9**. Yield 2.61 g (4.25 mmol, 96%) of an off-white powder. ¹H NMR (200 MHz, CDCl₃): $\delta = 8.88$ (s, br, 2H, CONH), 7.76–7.80 (m, 2H, ArH), 7.27–7.45 (m, 8H, ArH), 3.40–3.54 (m, 4H, SCH), 1.40 (d, $^3J_{\text{H,H}} = 6.8$ Hz, 12H, CH(CH₃)₂), 1.15 ppm (d, $^3J_{\text{H,H}} = 7.0$ Hz, 12H, CH(CH₃)₂). ¹³C NMR (50 MHz, CDCl₃): $\delta = 167.6$ (CONH), 146.0, 142.9, 130.4, 129.1, 128.3, 126.4, 126.3, 125.2, 125.0 (ArC), 40.8 (CH(CH₃)₂), 36.2 (CH(CH₃)₂), 23.0 (CH(CH₃)₂), 22.7 ppm (CH(CH₃)₂); MS (EI, 70 eV): *m/z* (%) = 612 (3, M⁺), 569 (25, M⁺-C₃H₇), 360 (69), 253 (58), 211 (73), 169 (49), 108 (100), 43 (3, C₃H₇⁺). IR (KBr): $\tilde{\nu} = 3261$ (st, N-H), 2962, 2924, 2863 (m, SC-H), 1660 (st, C=O), 1599, 1512 (m, Ar-C=C), 755 cm⁻¹ (s, Ar-H). Anal. Calcd for C₃₂H₄₀N₂O₂S₄: C, 62.71; H, 6.58; N, 4.57; S, 20.92. Found: C, 61.74; H, 6.38; N, 4.53; S, 20.83.

1,2-Bis(2,3-dimethoxybenzamido)benzene (12). 2,3-Dimethoxybenzoic acid (2.73 g, 15.0 mmol) and DMF (2 drops) were dissolved in SOCl₂ (10 mL). The solution was stirred for 12 h, and the volatiles were removed in vacuo to afford a white powder. The powder was dissolved in THF (20 mL) and added to a solution of 1,2-phenylene-

diamine (756 mg, 7.0 mmol) and NEt₃ (2.2 mL, 15.0 mmol) in THF (40 mL). The suspension obtained was stirred for 12 h at ambient temperature and NEt₃·HCl was filtered off. The solvent was removed in vacuo, and the resulting solid was washed with water and recrystallized from CH₂Cl₂/hexane to yield a white powder (2.90 g, 6.65 mmol, 95%). ¹H NMR (200 MHz, CDCl₃): $\delta = 9.97$ (s, 2H, CONH), 7.85–7.76 (m, 4H, ArH), 7.28 (dd, $^3J_{\text{H,H}} = 6.2$ Hz, $^4J_{\text{H,H}} = 3.3$ Hz, 2H, ArH), 7.17 (t, $^3J_{\text{H,H}} = 8.4$ Hz, 2H, ArH), 7.06 (dd, $^3J_{\text{H,H}} = 8.4$ Hz, $^4J_{\text{H,H}} = 1.8$ Hz, 2H, ArH), 3.87 (s, 6H, CH₃), 3.86 ppm (s, 6H, CH₃). ¹³C NMR (200 MHz, CDCl₃): $\delta = 164.2$ (CONH), 152.5, 147.7, 131.0, 126.3, 126.1, 125.4, 124.2, 122.9, 115.9 (ArC), 61.5, 56.0 ppm (CH₃). Anal. Calcd for C₂₄H₂₄N₂O₆: C, 66.05; H, 5.54; N, 6.42. Found: C, 65.83; H, 5.59; N, 6.22.

1,2-Bis(2,3-dimercaptobenzamido)ethane (H₄-1).¹⁰ ¹H NMR (200 MHz, [d₇]DMF): $\delta = 8.00$ (s, br, 2H, CONH), 6.83 (dd, 2H, ArH), 6.71 (dd, 2H, ArH), 6.32 (t, 2H, ArH), 5.17 (s, br, 4H, SH), 2.87 ppm (t, 4H, CH₂). ¹³C NMR (50 MHz, [d₇]DMF): $\delta = 170.0$ (CONH), 135.1, 134.0, 132.0, 126.3, 125.4 (ArC), 40.0 ppm (CH₂), only 5 of the expected 6 ArC signals were observed. MS (70 eV, EI): *m/z* (%) = 396 (31, M⁺), 364 (3, M⁺-SH), 228 (100), 199 (45), 168 (87), 78 (9, C₆H₆⁺), 34 (87, H₂S⁺). IR (KBr): $\tilde{\nu} = 3285$ (st, N-H), 3057, 2945 (s, Ar-H), 2528 (m, S-H), 1633 (st, C=O), 1572 (st, N-H), 1536 (st, Ar-C=C), 1442 cm⁻¹ (m, CH₂). Anal. Calcd for C₁₆H₁₆N₂O₂S₄: C, 48.46; H, 4.07; N, 7.06; S, 32.34. Found: C, 48.43; H, 4.37; N, 6.80; S, 31.46.

1,4-Bis(2,3-dimercaptobenzamido)benzene (H₄-2). Compound **9** (3.150 g, 5.14 mmol) and naphthalene (3.294 g, 25.70 mmol) were dissolved in THF (80 mL), and pieces of sodium (1.20 g, 52.17 mmol) were added. The mixture was stirred for 12 h at ambient temperature, and then methanol (10 mL) was added dropwise. After 10 min, the solvent was removed in vacuo, and the residue was dissolved in degassed water (40 mL) and washed with diethyl ether (3 × 20 mL). After the aqueous phase was filtered, hydrochloric acid (37%) was added dropwise to afford a white solid. The precipitate was filtered off, washed with water (2 × 20 mL) and diethyl ether (2 × 20 mL), and dried in vacuo to yield an off-white powder (1.98 g, 87%). ¹H NMR (200 MHz, [d₇]DMF): $\delta = 10.65$ (s, 2H, CONH), 7.99 (s, 4H, ArH), 7.77 (dd, $^3J_{\text{H,H}} = 7.8$ Hz, $^4J_{\text{H,H}} = 1.0$ Hz, 2H, ArH), 7.59 (dd, $^3J_{\text{H,H}} = 7.8$ Hz, $^4J_{\text{H,H}} = 1.0$ Hz, 2H, ArH), 7.28 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 2H, ArH), 5.38 ppm (s, br, 4H, SH). ¹³C NMR (50 MHz, [d₇]DMF): $\delta = 167.9$ (CONH), 137.1, 136.2, 134.7, 133.8, 131.9, 126.2, 125.7, 121.0 ppm (ArC). MS (70 eV, EI): *m/z* (%) = 444 (1, M⁺), 276 (100), 244 (54), 108 (88). IR (KBr): $\tilde{\nu} = 3279$ (st, N-H), 3145, 3048 (s, Ar-H), 2521 (m, S-H), 1641 (st, C=O), 1542 (st, N-H), 1608, 1571, 1516 cm⁻¹ (m, Ar-C=C). Anal. Calcd for C₂₀H₁₆N₂O₂S₄: C, 54.03; H, 3.63; N, 6.30; S, 28.84. Found: C, 54.38; H, 3.97; N, 6.00; S, 27.88.

1,2-(*R,R*)-Bis(2,3-dimercaptobenzamido)cyclohexane (H₄-3). Compound **10** (2.27 g, 3.67 mmol) and naphthalene (2.35 g, 18.35 mmol) were dissolved in THF (60 mL). Pieces of sodium (850 mg, 36.7 mmol) were added, the solution was stirred for 12 h at ambient temperature, and then methanol (10 mL) was added. After 10 min, the solvent was removed in vacuo, and the residue was dissolved in degassed water (40 mL). The aqueous phase was washed with diethyl ether (3 × 20 mL), filtered, and acidified with hydrochloric acid (37%) to afford a white solid. The precipitate was filtered off and washed with water (2 × 20 mL) and diethyl ether (2 × 20 mL). Drying in vacuo yielded H₄-3 as a white powder (1.40 g, 3.11 mmol, 85%). ¹H NMR (200 MHz, [d₇]DMF): $\delta = 8.46$ (d, $^3J_{\text{H,H}} = 7.6$ Hz, 2H, CONH), 7.56 (dd, 2H, ArH), 7.34 (dd, 2H, ArH), 7.03 (t, 2H, ArH), 5.80 (s, br, 4H, SH), 4.04 (s, br, 2H, NCH), 2.03 (d, br, 2H, CH₂), 1.78 (d, br, 2H, CH₂), 1.68 (d, br, 2H, CH₂), 1.39 ppm (d, br, 2H, CH₂). ¹³C NMR (50 MHz, [d₇]DMF): $\delta = 169.5$ (CONH), 135.6, 133.8, 131.8, 126.3, 125.3 (ArC), 53.6 (NCH), 32.5 (CH₂), 25.4 ppm (CH₂), only 5 of the expected 6 ArC resonances were observed. MS (MALDI): *m/z* = 451 [M⁺]. IR (KBr): $\tilde{\nu} = 3265$ (st, N-H), 3060 (s, Ar-H), 2930, 2857 (m, CH₂), 2529 (m, S-H), 1617 (st, C=O), 1572 (m, C=C), 1530 cm⁻¹ (m, N-

Table 3. Crystallographic Data for Li(PNP)₃[13], (PNP)₄[14], (Ph₄As)₂[16], and (PNP)₂[17]

| parameter | Li(PNP) ₃ [13]·3DMF·H ₂ O | (PNP) ₄ [14]·3DMF | (Ph ₄ As) ₂ [16]·4DMF | (PNP) ₂ [17]·2CH ₃ CN·2CH ₃ OH |
|--|--|---|--|---|
| formula | C ₁₆₅ H ₁₄₉ LiN ₁₂ O ₁₀ P ₆ S ₁₂ Ti ₂ | C ₂₁₃ H ₁₇₇ N ₁₃ O ₉ P ₈ S ₁₂ Ti ₂ | C ₁₀₂ H ₉₈ As ₂ N ₈ O ₁₀ S ₈ Ti ₂ | C ₁₂₀ H ₁₀₄ N ₈ O ₁₆ P ₄ Ti ₂ |
| fw | 3133.24 | 3790.96 | 2098.00 | 2133.79 |
| <i>T</i> (K) | 150(2) | 100(2) | 153(3) | 153(2) |
| crystal size (mm ³) | 0.50 × 0.07 × 0.07 | 0.38 × 0.16 × 0.14 | 0.23 × 0.06 × 0.06 | 0.12 × 0.04 × 0.02 |
| color of crystal | dark red | dark red | dark red | red-brown |
| space group | <i>P</i> 2 ₁ / <i>c</i> | <i>R</i> 3 <i>c</i> | <i>P</i> 1 | <i>P</i> 1 |
| wavelength (Å) | 1.541 84 | 1.541 78 | 0.710 73 | 0.710 73 |
| <i>a</i> (Å) | 17.8522(4) | 24.546(2) | 8.4004(10) | 14.038(3) |
| <i>b</i> (Å) | 23.0986(5) | 24.546(2) | 16.498(2) | 15.014(3) |
| <i>c</i> (Å) | 37.9215(9) | 112.885(10) | 17.952(2) | 15.241(3) |
| α (deg) | 90 | 90 | 80.544(2) | 105.879(4) |
| β (deg) | 99.417(2) | 90 | 76.820(2) | 100.689(4) |
| γ (deg) | 90 | 120 | 85.068(3) | 110.322(4) |
| <i>V</i> (Å ³) | 15426.6(6) | 58900(7) | 2386.6(5) | 2753.8(10) |
| <i>Z</i> | 4 | 12 | 1 | 1 |
| ρ _{calcd} (Mg m ⁻³) | 1.349 | 1.283 | 1.460 | 1.287 |
| μ (mm ⁻¹) | 3.495 | 2.989 | 1.095 | 0.272 |
| θ range (deg) | 2.36–70.17 | 2.22–70.05 | 1.84–30.08 | 1.46–23.50 |
| reflections coll. | 89 879 | 88 221 | 28 266 | 19 230 |
| <i>R</i> _{int} | 0.078 | 0.125 | 0.0399 | 0.1019 |
| data/restr./param. | 27 800/0/1922 | 12 393/21/786 | 13 819/0/608 | 8128/0/681 |
| GOF | 0.938 | 1.040 | 1.007 | 0.977 |
| <i>R</i> ₁ , w <i>R</i> ² [<i>I</i> ≥ 2σ(<i>I</i>)] | 0.0522, 0.1330 | 0.0886, 0.2439 | 0.0464, 0.1013 | 0.0877, 0.2141 |
| <i>R</i> ₁ , w <i>R</i> ² (all data) | 0.0786, 0.1427 | 0.1258, 0.2790 | 0.0746, 0.1107 | 0.1717, 0.2654 |
| max. peak/hole (e Å ⁻¹) | +1.737/−0.438 | +1.723/−0.723 | +0.798/−0.459 | +1.432/−0.399 |

H). Anal. Calcd for C₂₀H₂₂N₂O₂S₄: C, 53.31; H, 4.92; N, 6.22; S, 28.46. Found: C, 53.15; H, 4.77; N, 5.85; S, 28.59.

1,2-Bis(2,3-dimercaptobenzamido)benzene (H₄-4). Compound **11** (2.50 g, 4.08 mmol) and naphthalene (3.42 g, 20.40 mmol) were dissolved in THF (60 mL), and pieces of sodium (938 mg, 40.80 mmol) were added. The solution was stirred for 12 h at ambient temperature, and then methanol (10 mL) was added. After 10 min, the solvent was removed in vacuo, and the residue was dissolved in degassed water (40 mL). The aqueous phase was washed with diethyl ether (3 × 20 mL), filtered, and acidified with hydrochloric acid (37%) to afford a white solid. The precipitate was filtered off and washed with water (2 × 20 mL) and diethyl ether (2 × 20 mL). Drying in vacuo yielded H₄-4 as a white powder (1.47 g, 3.30 mmol, 81%). ¹H NMR (200 MHz, [d₇]DMF): δ = 10.08 (s, 2H, CONH), 7.81–7.10 (m, 10H, ArH), 5.04 ppm (s, br, 4H, SH). ¹³C NMR (50 MHz, [d₇]DMF): δ = 187.9 (CONH), 132.3, 131.8, 129.6, 128.4, 126.4, 126.3, 126.2, 126.1, 125.9 ppm (ArC). MS (MALDI): *m/z* (%) = 444 (100, M⁺). IR (KBr): $\tilde{\nu}$ = 3348, 3201 (st, N–H), 2518 (m, S–H), 1662 (st, C=O), 1508 (m, Ar–C=C), 753 cm⁻¹ (st, Ar–H). Anal. Calcd for C₂₀H₁₆N₂O₂S₄: C, 54.03; H, 3.63; N, 6.30; S, 28.84. Found: C, 54.21; H, 3.84; N, 5.94; S, 28.29.

1,2-Bis(2,3-dihydroxybenzamido)benzene (H₄-5). Compound **12** (1.50 g, 3.43 mmol) was dissolved in CH₂Cl₂ (60 mL), and BBr₃ (4.30 g, 17.15 mmol) was added at 0 °C. The suspension was stirred for 12 h at room temperature, and the volatiles were removed in vacuo. The resulting solid was suspended in water (50 mL) and refluxed for 2 h. A white precipitate formed, which was filtered off, washed with water and diethyl ether, and dried in vacuo to give H₄-5 as a white powder (1.13 g, 2.98 mmol, 87%). ¹H NMR (400 MHz, [d₇]DMF): δ = 10.35 (s, 2H, CONH), 7.72 (dd, ³*J*_{H,H} = 5.9 Hz, ⁴*J*_{H,H} = 3.4 Hz, 2H, ArH), 7.44 (dd, ³*J*_{H,H} = 8.2 Hz, ⁴*J*_{H,H} = 1.4 Hz, 2H, ArH), 7.30 (dd, ³*J*_{H,H} = 5.9 Hz, ⁴*J*_{H,H} = 3.4 Hz, 2H, ArH), 6.97 (dd, ³*J*_{H,H} = 8.2 Hz, ⁴*J*_{H,H} = 1.4 Hz, 2H, ArH), 6.75 (t, ³*J*_{H,H} = 8.2 Hz, 2H, ArH), 4.98 ppm (s, 4H, OH). ¹³C NMR (100 MHz, [d₇]DMF): δ = 169.1 (CONH), 149.2, 146.6, 136.4, 131.0, 118.8, 117.3, 115.3, 110.9 ppm (ArC), only 8 of the expected 9 ArC resonances were observed. Anal. Calcd for C₂₀H₁₆N₂O₆: C, 63.16; H, 4.24; N, 7.37. Found: C, 62.65; H, 4.73; N, 7.52.

Li(PNP)₃[Ti₂(1)₃] Li(PNP)₃[13]. ¹⁵Li NMR (400 MHz, [d₇]DMF): δ = 8.85 (s, 6H, CONH), 7.98–7.91 (m, 16H, PNP–H), 7.89–7.82

(m, 64H, PNP–H), 7.34 (dd, ³*J*_{H,H} = 7.6 Hz, ⁴*J*_{H,H} = 1.5 Hz, 6H, ArH), 7.00 (dd, ³*J*_{H,H} = 7.6 Hz, ⁴*J*_{H,H} = 1.5 Hz, 6H, ArH), 6.66 (t, ³*J*_{H,H} = 7.6 Hz, 6H, ArH), 3.46 ppm (t, 12H, CH₂). ¹³C NMR (100 MHz, [d₇]DMF): δ = 169.3 (CONH), 156.3, 151.1, 135.3, 134.4, 133.8, 131.9, 129.2, 129.1, 125.1, 122.3, 121.9 (ArC), 40.1 ppm (CH₂). MS (ESI, neg. ions): *m/z* = 424.1 ((H[Ti₂(1)₃]³⁻), 604.1, ((PNP)[Ti₂(1)₃]³⁻). Anal. Calcd for solvent-free Li(PNP)₃[Ti₂(1)₃] C₁₅₆H₁₂₆LiN₉O₆P₆S₁₂Ti₂: C, 64.70; H, 4.39; N, 4.35; S, 13.28. Found: C, 65.04; H, 4.54; N, 4.39; S, 13.72.

(PNP)₄[Ti₂(2)₃] (PNP)₄[14]. A sample of [Ti(OC₂H₅)₄] (17 mg, 0.075 mmol) was added to a solution of H₄-2 (50 mg, 0.113 mmol) and Li₂CO₃ (6 mg, 0.075 mmol) in degassed methanol (20 mL). The solution was stirred for 12 h at ambient temperature and filtered. Addition of (PNP)Cl (86 mg, 0.15 mmol) to the filtrate yields a brown precipitate, which was isolated by filtration, washed with methanol, and dried in vacuo. Yield 98 mg (0.027 mmol, 73%) of red-brown powder. ¹H NMR (500 MHz, [d₇]DMF): δ = 11.18 (s, 6H, CONH), 7.82 (s, 12H, ArH), 7.77–7.68 (m, 72H, PNP–H), 7.60–7.56 (m, 48H, PNP–H), 7.48 (dd, ³*J*_{H,H} = 7.5 Hz, ⁴*J*_{H,H} = 1.5 Hz, 6H, ArH), 7.10 (dd, ³*J*_{H,H} = 7.5 Hz, ⁴*J*_{H,H} = 1.5 Hz, 6H, ArH), 6.74 ppm (t, ³*J*_{H,H} = 7.5 Hz, 6H, ArH). ¹³C NMR (125 MHz, [d₇]DMF): δ = 166.5 (CONH), 155.9, 150.3, 135.5, 133.9, 133.3, 132.6, 132.5, 129.7, 129.7, 128.5, 128.0, 127.2, 125.0, 121.2, 119.7 ppm (ArC). MS (ESI, neg. ions): *m/z* = 651.3 ([((PNP)[Ti₂(2)₃]³⁻), 1248.0 ([((PNP)₂][Ti₂(2)₃]²⁻). Anal. Calcd for solvent-free (PNP)₄[Ti₂(2)₃] C₂₀₄H₁₅₆N₁₀O₆P₈S₁₂Ti₂: C, 68.60; H, 4.40; N, 3.92; S, 10.77. Found: C, 68.21; H, 4.73; N, 4.33; S, 10.38.

(Ph₄As)₄[Ti₂(3)₃] (Ph₄As)₄[15]. A sample of [Ti(OC₂H₅)₄] (17 mg, 0.074 mmol) was added to a solution of H₄-3 (50 mg, 0.111 mmol) and Li₂CO₃ (6 mg, 0.074 mmol) in degassed methanol (20 mL). The solution was stirred for 12 h at ambient temperature and filtered. Addition of (Ph₄As)Cl (63 mg, 0.15 mmol) to the filtrate yielded a brown precipitate, which was isolated by filtration, washed with methanol, and dried in vacuo. Yield 69 mg (0.022 mmol, 60%) of a red-brown powder. ¹H NMR (400 MHz, [d₇]DMF): δ = 8.63 (d, ³*J*_{H,H} = 6.2 Hz, 6H, CONH), 7.97–7.80 (m, 20H, Ph₄As–H), 7.31 (dd, ³*J*_{H,H} = 7.5 Hz, ⁴*J*_{H,H} = 1.4 Hz, 6H, ArH), 7.08 (dd, ³*J*_{H,H} = 7.5 Hz, ⁴*J*_{H,H} = 1.4 Hz, 6H, ArH), 6.68 (t, ³*J*_{H,H} = 7.5 Hz, 6H, ArH), 4.34 (s, br, 6H, CH), 2.13–1.19 ppm (m, br, 24H, CH₂). ¹³C NMR (100 MHz, [d₇]DMF): δ = 165.2 (CONH), 157.3, 151.1, 139.6, 139.2, 138.7, 131.5, 130.0, 129.4, 128.8, 125.2, 124.1, 122.7 (ArC), 53.6. (CH), 34.4,

26.8 ppm (CH₂). MS (ESI, neg. ions): $m/z = 478$ ([H[Ti₂(**3**)₃]]³⁻), 606 ([Ph₄As][Ti₂(**3**)₃]]³⁻), 718 ([H₂[Ti₂(**3**)₃]]²⁻). Anal. Calcd for solvent-free (Ph₄As)₄[Ti₂(**3**)₃] C₁₆₆H₁₆₄As₄N₆O₆S₁₂Ti₂: C, 63.11; H, 4.55; N, 2.83; S, 12.96. Found: C, 63.35; H, 4.27; N, 3.03; S, 13.54.

(Ph₄As)₂[Ti₂(4**)₂(OCH₃)₂] (Ph₄As)₂[**16**].** A sample of [Ti(OC₂H₅)₄] (26 mg, 0.113 mmol) was added to a solution of H₄-**4** (50 mg, 0.113 mmol) and Li₂CO₃ (6 mg, 0.075 mmol) in degassed methanol (20 mL). The solution was stirred for 12 h at ambient temperature and filtered. Addition of (Ph₄As)Cl (54 mg, 0.113 mmol) to the filtrate yielded a brown precipitate, which was isolated by filtration, washed with methanol (3 × 20 mL), and dried in vacuo. Yield 45 mg (0.025 mmol, 67%). ¹H NMR (400 MHz, [d₇]DMF): δ = 9.77 (s, 4H, CONH), 8.32 (dd, ³J_{H,H} = 6.2 Hz, ⁴J_{H,H} = 3.7 Hz, 4H, ArH), 7.15 (dd, ³J_{H,H} = 6.2 Hz, ⁴J_{H,H} = 3.7 Hz, 4H, ArH), 7.11 (dd, ³J_{H,H} = 7.5 Hz, ⁴J_{H,H} = 1.4 Hz, 4H, ArH), 6.92 (dd, ³J_{H,H} = 7.5 Hz, ⁴J_{H,H} = 1.4 Hz, 4H, ArH), 6.79 (t, ³J_{H,H} = 7.5 Hz, 4H, ArH), 4.60 ppm (s, 6H, CH₃O). ¹³C NMR (100 MHz, [d₇]DMF): δ = 168.3 (CONH), 155.6, 144.8, 135.6, 135.1, 134.4, 134.2, 131.7, 130.4, 130.3, 130.2, 124.4, 124.1, 123.8 (ArC), 69.3 ppm (CH₃O). MS (ESI, neg. ions): $m/z = 519$ ([Ti₂(**4**)₂(OCH₃)₂]²⁻). Anal. Calcd for solvent-free (Ph₄As)₂[Ti₂(**4**)₂(OCH₃)₂] C₉₀H₇₀As₂N₄O₆S₈-Ti₂: C, 59.87; H, 3.91; N, 3.10; S, 14.20. Found: C, 60.33; H, 3.84; N, 2.87; S, 14.54.

(PNP)₂[Ti₂(5**)₂(OCH₃)₂] (PNP)₂[**17**].** A sample of H₄-**5** (50 mg, 0.132 mmol) was suspended in methanol (20 mL). Li₂CO₃ (5 mg, 0.066 mmol) and [TiO(acac)₂] (35 mg, 0.132 mmol) were added, and the obtained orange solution was stirred for 12 h at room temperature. (PNP)Cl (76 mg, 0.132 mmol) was added, and the resulting precipitate was filtered off, washed with methanol, and dried in vacuo to afford an orange solid (89 mg, 0.045 mmol, 68%). ¹H NMR (400 MHz, [d₇]DMF): δ = 10.63 (s, 2H, CONH), 7.87 (dd, ³J_{H,H} = 5.8 Hz, ⁴J_{H,H} = 3.6 Hz, 4H, ArH), 7.78–7.71 (m, 36H, PNP-H), 7.63–7.58 (m, 24H, PNP-H), 7.26–7.23 (m, 8H, ArH), 6.53 (t, ³J_{H,H} = 7.8 Hz, 4H, ArH), 6.34 (dd, ³J_{H,H} = 7.5 Hz, ⁴J_{H,H} = 1.5 Hz, 4H, ArH), 4.43 (s, 6H, CH₃O). MS (ESI, neg. ions): $m/z = 455$ ([Ti₂(**5**)₂(OCH₃)₂]²⁻). Anal. Calcd for solvent-free (PNP)₂[Ti₂(**5**)₂(OCH₃)₂] C₁₁₄H₉₀N₆O₁₄P₄Ti₂: C, 68.89; H, 4.56; N, 4.23. Found: C, 69.44; H, 4.59; N, 5.02.

X-ray Crystallography. X-ray diffraction data (Table 3) were collected on a Bruker AXS diffractometer equipped with a rotating anode generator and with Mo Kα ((Ph₄As)₂[**16**]·4DMF, (PNP)₂[**17**]·2CH₃CN·2CH₃OH), or Cu Kα radiation (Li(PNP)₃[**13**]·3DMF·H₂O, (PNP)₄[**14**]·3DMF). All raw data were corrected for absorption. The structure solutions were found with SHELXS,²² and the refinement was carried out with SHELXL²³ using anisotropic thermal parameters for all non-hydrogen atoms (see below for exceptions). Hydrogen atoms were added to the structure models on calculated positions and were refined as rigid atoms or were unrefined. One PNP cation in (PNP)₄[**14**]·3DMF is disordered around a special position. The positional parameters of this molecule were refined with one common isotropic thermal parameter. The solvent molecules in (PNP)₂[**17**]·2CH₃CN·2CH₃OH are disordered, and the corresponding positional parameters have been refined with isotropic thermal parameters.

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Supporting Information Available: X-ray crystallographic files for Li(PNP)₃[**13**]·3DMF·H₂O, (PNP)₄[**14**]·3DMF, (Ph₄As)₂[**16**]·4DMF, and (PNP)₂[**17**]·2CH₃CN·2CH₃OH (four CIF files). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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