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Helical Complexes Containing Diamide-Bridged Benzene-*o*-dithiolato/Catecholato Ligands

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Abstract: The benzene-*o*-dithiol/catechol ligands H_4-**2** and H_4-**3** react with $[TiO(acac)_2]$ to give the dinuclear, double-stranded anionic complexes $[Ti_2(L)_2(\mu\text{-}OCH_3)_2]^{2-}$ ($[\mathbf{22}]^{2-}$, L = $\mathbf{2}^{4-}$; $[\mathbf{23}]^{2-}$, L = $\mathbf{3}^{4-}$). NMR spectroscopic investigations reveal that the complex anion $[Ti_2(\mathbf{2})_2(\mu\text{-}OCH_3)_2]^{2-}$ is formed as a mixture of three of four possible isomers/pairs of enantiomers, whereas only one isomer of the complex anion $[Ti_2(\mathbf{3})_2(\mu\text{-}OCH_3)_2]^{2-}$ is obtained. The crystal structure analysis of $(PNP)_2$-$[Ti_2(\mathbf{3})_2(\mu\text{-}OCH_3)_2]$ shows a parallel orientation of the ligand strands, whereas the structure determination for $(AsPh_4)_2[Ti_2(\mathbf{2})_2(\mu\text{-}OCH_3)_2]$ does not yield conclusive results about the orientation of the ligand strands due the presence of different isomers in solution, the possible co-crystallisation of different isomers and severe disorder in the crystal. NMR spectroscopy shows that ligand H_4-**3** reacts at elevated temperature with $[TiO(acac)_2]$ to give the triple-stranded helicate $(PNP)[Ti_2(\mathbf{3})_3]$ ($(PNP)_4[\mathbf{24}]$) as a mixture of two isomers, one with a parallel orientation of the ligand strands and one with an antiparallel orientation. Exclusively the triple-stranded helicates $[Ti_2(L)_3]^{4-}$ ($[\mathbf{25}]^{4-}$, L = $\mathbf{1}^{4-}$; $[\mathbf{26}]^{2-}$, L = $\mathbf{4}^{4-}$) are formed in the reaction of ligands H_4-**1** and H_4-**4** with $[TiO(acac)_2]$. The molecular structures of $Na(PNP)_3[Ti_2(\mathbf{1})_3]\cdot CH_3OH\cdot H_2O\cdot Et_2O$ ($Na(PNP)_3[\mathbf{25}]\cdot CH_3OH\cdot H_2O\cdot Et_2O$) and $Na_{1.5}(PNP)_{6.5}[Ti_2(\mathbf{4})_3]_2\cdot 3\,DMF$ ($Na_{1.5}(PNP)_{6.5}[\mathbf{26}]_2\cdot 3\,DMF$) reveal a parallel orientation of the ligand strands in both complexes, which is retained in solution. The sodium cations present in the crystal structures lead to two different kinds of aggregation in the solid state. Na-[**25**]-Na-[**25**]-Na polymeric chains are formed from compound $Na(PNP)_3[\mathbf{25}]$, with the sodium cations coordinated by the carbonyl groups of two ligand strands from two different $[Ti_2(\mathbf{1})_3]^{4-}$ ions in addition to solvent molecules. In contrast to this, two $[Ti_2(\mathbf{4})_3]^{4-}$ ions are connected by a sodium cation that is coordinated by the three *meta* oxygen atoms of the catecholato groups of each complex tetraanion to form a central $\{NaO_6\}$ octahedron in the anionic pentanuclear complex $\{[\mathbf{26}]\text{-Na-}[\mathbf{26}]\}^{7-}$.

Keywords: directional ligands · helical structures · O,S donor ligands · self-assembly · titanium

Introduction

The spontaneous self-assembly of supramolecular coordination compounds has attracted much interest over the last few decades,[1] and several structural motifs have been prepared by transition-metal-directed self-assembly reactions.[2] Among these, metallohelicates have attracted special interest due to their presence in nature.[3] Raymond et al. isolated the first triple-stranded helicate $[Fe_2(RA)_3]$ (H_2RA = rhodothorulic acid) that contains exclusively oxygen donor functions from hydroxamato groups.[4]

The first structurally characterised metallohelicate contains two tris(bipyridine) ligands and three Cu^I ions and was reported by Lehn et al. in 1987.[5] In the following years, helicate chemistry was dominated by ligands with nitrogen donors like oligopyrimidines. Later, the groups of Raymond,[6] Stack[7] and Albrecht[8] prepared a series of dicatechol ligands that have been used to prepare dinuclear, triple-stranded helicates. Besides helicates, tetranuclear clusters of the type $[M_4L_6]^{n-}$ have been prepared from dicatechol ligands and selected metal ions, and these clusters have been used as host molecules in host–guest chemistry.[9]

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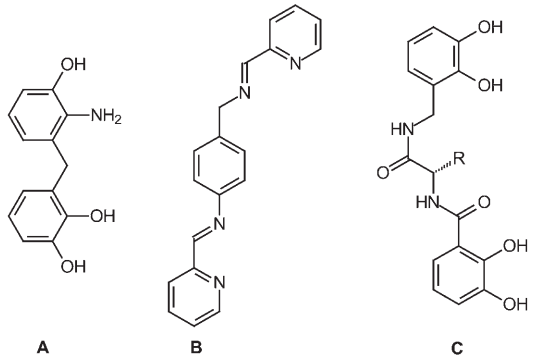
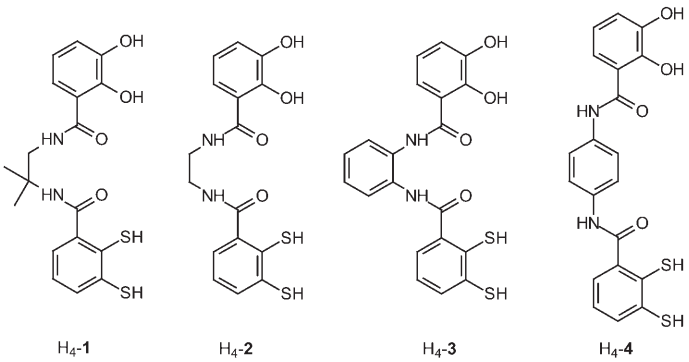
Sulfur donor groups remain comparatively rare in supramolecular chemistry. In 1995, we described a method for the *ortho* functionalisation of benzene-1,2-dithiol that led to the preparation of the first bis- and tris(benzene-*o*-dithiol) ligands.[10] Some dinuclear, non-helical nickel complexes[11] and a tetranuclear metallacycle[12] have since been described with this type of ligand, and the first triple-stranded helicates with bis(benzene-*o*-dithiolato) ligands have been described recently.[13]

Triple-stranded helicates built from ligands containing different donor units (a type of directional ligand) are rare. The orientation of a directional ligand in a dinuclear complex is of special interest since both complexes with stereoisomeric metal centres (Λ, Δ isomers) and regioisomeric complexes (parallel or antiparallel orientation of the ligands) can be formed. Several directional ligands have been used successfully for the preparation of dinuclear helical complexes. For instance, Albrecht et al. have described triple-stranded helicates build from the catechol/aminophenol ligand **A**.[14] A homodinuclear complex with an antiparallel orientation of the ligands was obtained from the reaction of **A** with Ga^{III} or Ti^{IV}, whereas the reaction of **A** with a mixture of Ga^{III} and Ti^{IV} gave a heterodinuclear complex with a parallel orientation of the ligand strands. In addition,



directional ligands that have identical donor groups but an asymmetric spacer between them (**B**[15] and **C**[16]) are known. An antiparallel orientation of the ligand strands was observed in homodinuclear double-stranded silver complexes with ligand **B**, which was attributed mainly to the geometric situation within the ligand,[15] and Albrecht et al. have described a series of unsymmetrical, amino-acid-bridged dicatechol ligands of type **C** that form only dinuclear double-stranded complexes with Ti^{IV}; no dinuclear, triple-stranded helicates were observed.[16]

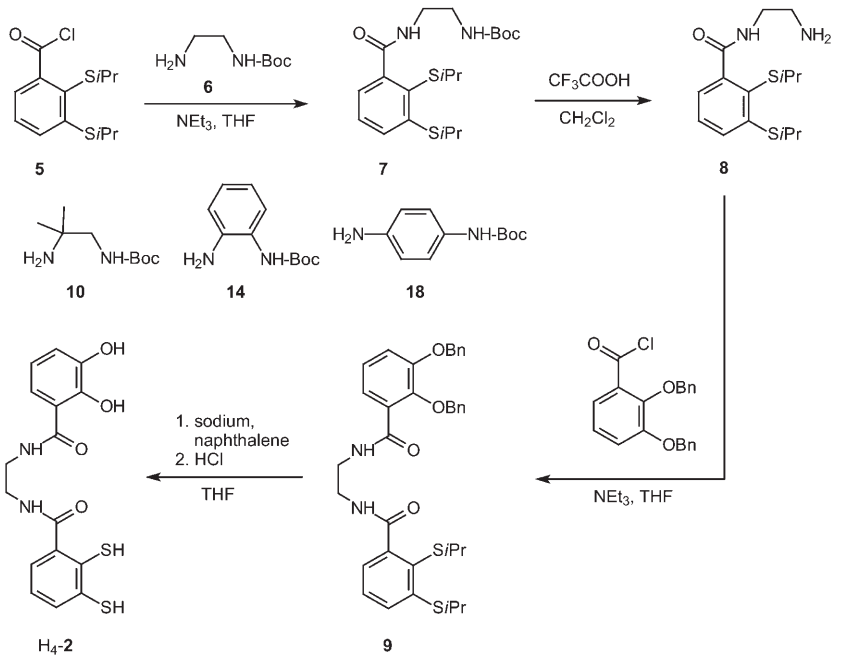
We recently reported the synthesis of the first mixed benzene-*o*-dithiol/catechol ligand H_4-**1**,[17] which is a new type of directional ligand that contains two different donor groups with an unsymmetrical spacer between them. Our interest in the coordination chemistry of ligands containing the benzene-*o*-dithiolato donor unit was triggered by the unique features of tris(benzene-1,2-dithiolato) complexes. For example, complexes of the type $[M(bdt)_3]^{n-}$ (bdt = benzene-



1,2-dithiolato dianion; M = Mo,[18] W[19]) can adopt a pseudo-octahedral ($[Mo^{V}(bdt)_3]^{-}$,[18b] $[W^{V}(bdt)_3]^{-}$[19b]) or a trigonal-prismatic ($[Mo^{VI}(bdt)_3]$,[18a] $[W^{VI}(bdt)_3]$)[19c] coordination geometry. Incorporation of molybdenum or tungsten into dinuclear, triple-stranded complexes with ligands like H_4-**1** could lead to a helicate with two octahedral metal centres or to a non-helical complex containing at least one trigonal-prismatic $\{M^{VI}S_6\}$ ($M = W^{VI}$ or Mo^{VI}) metal centre. This, however, would require the parallel orientation of the ligand strands in the dinuclear, triple-stranded complex. In a first study we have demonstrated that ligand H_4-**1** reacts with Ti^{IV} to form a triple-stranded, dinuclear helicate with a parallel orientation of the ligand strands.[17] However, since H_4-**1** is directional with respect to the donor groups and the spacer unit, the reasons for the parallel orientation of the ligand strands remained speculative. With this contribution we expand our study of the coordination chemistry of mixed benzene-*o*-dithiolato/catecholato ligands and report on the Ti^{IV} coordination chemistry of the ligands H_4-**2**–H_4-**4**, which contain a non-directional, symmetrical diamide bridge between the donor groups.

Results and Discussion

Ligand synthesis: Scheme 1 depicts, as an example, the preparation of ligand H_4-**2** using a procedure which is similar to the method developed by Albrecht et al. for the synthesis of ligands of type **C**.[20] The synthesis starts from 2,3-di(isopropylmercapto)benzoic acid chloride (**5**), which we have reported previously.[10] Reaction of **5** with the single *tert*-butyloxycarbonyl(Boc)-protected ethylenediamine **6**[21] in the presence of NEt_3 yields compound **7**. Removal of the Boc group by treatment with trifluoroacetic acid liberates the free amine **8**. Compounds of type **8** with aliphatic spacers between the nitrogen atoms have been isolated in their deprotonated form, while the compounds with aromatic spacers are normally isolated as hydrochlorides. Compound **8** reacts with 2,3-di(benzyloxy)benzoic acid chloride[22] to give the S- and O-alkylated ligand precursor **9**. Both the benzyl and the isopropyl protection groups can be removed simultaneously by treatment with sodium/naphthalene in THF to give H_4-**2** after hydrolysis with HCl/H_2O. Li-



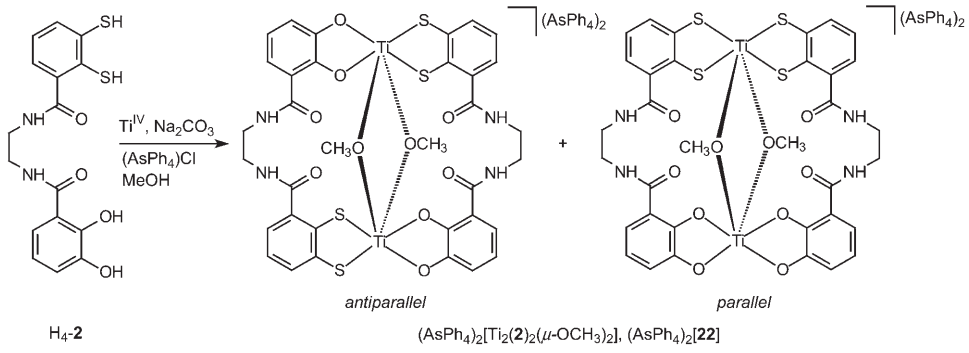
Scheme 1. Preparation of ligand H_4-**2**.

gands of type H_4-**2** are only soluble in DMF and are therefore easily purified by washing with water and diethyl ether. Ligands H_4-**1**,[17] H_4-**3** and H_4-**4** were synthesised following the same procedure, the only difference being the use of the singly Boc-protected amines **10** (for H_4-**1**), **14** (for H_4-**3**) and **18** (for H_4-**4**) (Scheme 1) instead of **6** for the initial coupling with the acid chloride **5**.

Synthesis of the dinuclear, double-stranded complex $(AsPh_4)_2[Ti_2(2)_2(\mu\text{-}OCH_3)_2]$ ($(AsPh_4)_2$[22]): The reaction of three equivalents of ligand H_4-**2** with two equivalents of $[TiO(acac)_2]$ and Na_2CO_3 in methanol gave a brownish solution containing the double-stranded, dinuclear complex $Na_2[Ti_2(\mathbf{2})_2(\mu\text{-}OCH_3)_2]$ (Na_2[**22**]) rather than the hoped-for triple-stranded, dinuclear helical complex $Na_4[Ti_2(\mathbf{2})_3]$ (Scheme 2). No evidence for the formation of the triple-stranded helicate $Na_4[Ti_2(\mathbf{2})_3]$ was found even after increasing the ligand:metal ratio. This is in contrast to the behaviour of the analogous dicatecholato and bis(benzene-*o*-dithiolato) ligands with the same topology as H_4-**1**, which both form dinuclear, triple-stranded helicates of type $[M_2L_3]^{n-}$ when reacted in a metal/ligand ratio of 2:3 ($M=Fe^{III}$, dicatecholato ligand;[7a] $M=Ti^{IV}$, bis(benzene-*o*-dithiolato ligand[13a]). We have not been able to isolate Na_2[**22**] in an analytically pure form or to crystallise the compound. Recrystallisation of Na_2[**22**] in the presence of $(AsPh_4)Cl$ from a methanol/diethyl ether solution gave, after cation exchange, analytically pure $(AsPh_4)_2$[**22**] as a red powder which was fully characterised by elemental analysis, mass spectrometry and NMR spectroscopy.

Owing to the directionality of the ligand $\mathbf{2}^{4-}$ two regioisomeric complexes $[\mathbf{22}]^{2-}$ can be formed, one with an antiparallel orientation of the ligand strands and one with a parallel orientation (Scheme 2). Apart from these parallel and antiparallel regioisomers, a total of seven stereoisomers of the complex dianion $[\mathbf{22}]^{2-}$ are possible due to the chirality of the (distorted) octahedral titanium centres. Three stereoisomers result from the antiparallel orientation of the ligand strands, while the parallel orientation leads to another four stereoisomers (Figure 1). Six of these seven stereoisomers form three pairs of enantiomers, while no enantiomer exists for the Δ,Λ complex with an antiparallel orientation of the ligand strands (Figure 1).

If all isomers coexist in solution, a maximum of four sets of resonances will be observed in the NMR spectra (one for each isomer/pair of enantiomers). A similar situation has been described by Albrecht, who reported a complex anion composed of two Ti^{IV} ions coordinated by two phenylalanine-bridged (directional) dicatecholato ligands and two bridging methoxy co-ligands.[16] The ^{1}H NMR spectrum of $(AsPh_4)_2$[**22**] shows two singlets for the protons of the methoxy groups at $\delta=4.38$ and 4.52 ppm, 12 doublets and six triplets for the aromatic protons of the benzene-*o*-dithiolato and catecholato groups (Figure 2), and six signals for the aliphatic CH_2 protons of the ethylene bridge. This clearly shows that three of the four possible isomers (or pairs of enantiomers) are formed



Scheme 2. Preparation of $(AsPh_4)_2[Ti_2(\mathbf{2})_2(\mu\text{-}OCH_3)_2]$ and the two possible regioisomers of the complex dianion.

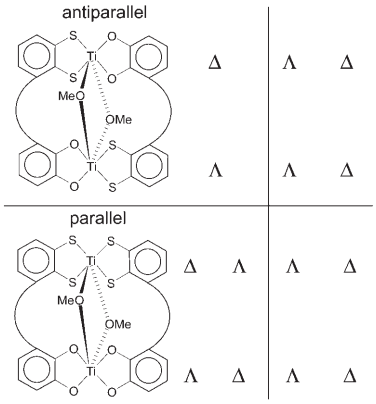


Figure 1. Schematic representation of the possible stereoisomers of complex anion $[\mathbf{22}]^{2-}$.

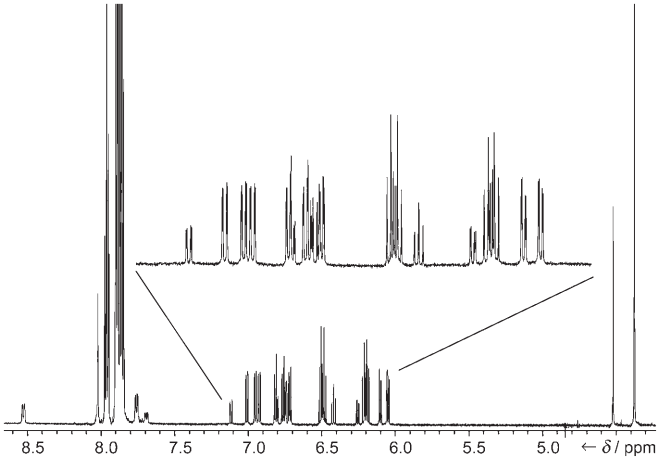


Figure 2. Part of the ^{1}H NMR spectrum of $(AsPh_4)_2[\mathbf{22}]$ (in $[D_7]$DMF) showing 12 doublets and six triplets for the aromatic protons of the ligand strands.

during the preparation of $(AsPh_4)_2[\mathbf{22}]$ and coexist in solution. Each of these isomers (or pairs of enantiomers) gives rise to four doublets and two triplets for the aromatic protons of the ligand strands and two signals for the methylene protons of the bridging ethylene group. The mixture of three isomers must contain at least one complex with a parallel and one complex with an antiparallel orientation of the ligand strands.

Integration of the signal intensities in the ^{1}H NMR spectrum of $(AsPh_4)_2[\mathbf{22}]$ shows that two main isomers (46 and 35%) and one minor isomer (19%) are present in solution. Unfortunately, we have not been able to assign the stereoisomers based on the NMR spectra. The formation of three isomers (or pairs of enantiomers) is also corroborated by the observation of 36 signals for the aromatic carbon atoms of the benzene-*o*-dithiolato and catecholato groups (12 for each isomer or pair of enantiomers) in the ^{13}C NMR spectrum of $(AsPh_4)_2[\mathbf{22}]$.

Only four resonances for the amide NH protons of $[\mathbf{22}]^{2-}$ are observed at ambient temperature (two for each isomer or pair of enantiomers). This appears to contradict the presence of three isomers (or pairs of enantiomers) of $(AsPh_4)[\mathbf{22}]$ in solution. However, the expected six NH resonances are detected at low temperature (Figure 3).

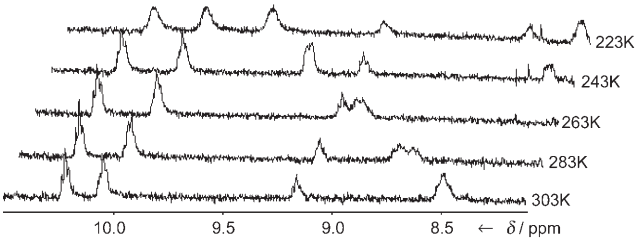


Figure 3. Variable temperature ^{1}H NMR spectra of $(AsPh_4)_2[\mathbf{22}]$ (in $[D_7]$DMF) showing four NH resonances at ambient temperature (303 K) and six NH resonances at low temperature (223 K).

It has been demonstrated that the amide proton resonance in the ^{1}H NMR spectrum is a sensitive probe for the detection of hydrogen bonds between it and the donor groups (O and S) of the adjacent benzene-*o*-dithiolato and catecholato groups.[17] Strong N–H···O/S hydrogen bonds give rise to a downfield shift of the NH resonances relative to the uncoordinated, protonated ligand. The NH resonances of ligand H_4-**2** appear as singlets at $\delta = 9.10$ (catechol amide) and 8.83 ppm (benzene-*o*-dithiol amide) in the ^{1}H NMR spectrum. We have not been able to assign the six NH resonances at $\delta = 10.06$, 9.82, 9.53, 9.00, 8.33 and 8.10 ppm that are observed in the ^{1}H NMR spectrum of $(AsPh_4)_2[\mathbf{22}]$ at low temperature (Figure 3), therefore it remains open to speculation which kind of hydrogen bonds (N–H···O or N–H···S) are formed in the complex anion $[\mathbf{22}]^{2-}$.

The NMR spectra of $(AsPh_4)_2[\mathbf{22}]$ do not become simpler upon heating or extended standing of solutions of the complex at room temperature, thus indicating that the isomers do not differ significantly in their energy. Red single crystals of $(AsPh_4)_2[\mathbf{22}]\cdot 2\,CH_3OH$ were obtained by slow diffusion of diethyl ether into a methanolic solution of $(AsPh_4)_2[\mathbf{22}]$. Compound $(AsPh_4)_2[\mathbf{22}]\cdot 2\,CH_3OH$ crystallises in the centrosymmetric space group $P\bar{1}$ with $Z = 1$. The complex dianion $[\mathbf{22}]^{2-}$ resides on a crystallographic inversion centre. Provided that there is no crystallographic disorder, the complex dianions $[\mathbf{22}]^{2-}$ with a parallel orientation of the ligand strands, which are present in solution, cannot lie on an inversion centre. The detection of $[\mathbf{22}]^{2-}$ on a crystallographic inversion centre could therefore indicate that only complex anions with an antiparallel orientation of the ligand strands are present in the crystals of $(AsPh_4)_2[\mathbf{22}]\cdot 2\,CH_3OH$. Alternatively, all three isomers present in solution could co-crystallise in a disordered lattice. Unfortunately, the latter situation was observed with crystals of $(AsPh_4)_2[\mathbf{22}]\cdot 2\,CH_3OH$. The dianion $[\mathbf{22}]^{2-}$ 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 in $[\mathbf{22}]^{2-}$ and thus the orientation of the ligand strands cannot be determined. In addition, no reliable bond distances or angles can be determined. Since anion $[\mathbf{22}]^{2-}$ possesses a crystallographic inversion centre in the middle of the $[Ti_2(\mu\text{-}OCH_3)_2]$ ring in the crystal lattice, it can be assumed that only anions with opposite configurations at the two metal centres (*meso* complexes) crystallise. However, such *meso* complex dianions can form with both a parallel or antiparallel orientation of the ligand strands. Thus, the crystal structure determination only confirms the chemical composition of the dianion to be $[Ti_2(\mathbf{2})_2(\mu\text{-}OCH_3)_2]^{2-}$. One of the isomers of $[\mathbf{22}]^{2-}$ present in the crystal structure of $(AsPh_4)_2[\mathbf{22}]\cdot 2\,CH_3OH$ is depicted in Figure 4. This is the isomer with the antiparallel orientation of the ligand strands and opposite configurations at the metal centres that corresponds best to the crystallographically observed site symmetry.

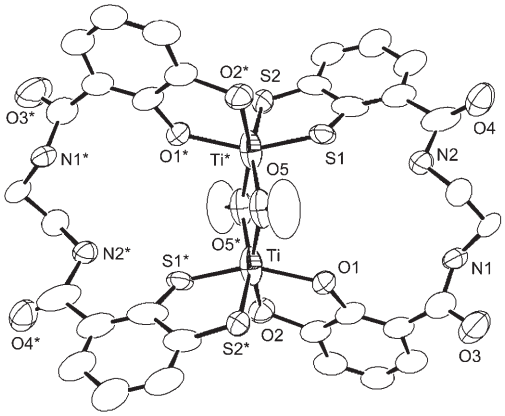


Figure 4. ORTEP drawing of the centrosymmetric $[\mathbf{22}]^{2-}$ anion present in the crystal structure of $(AsPh_4)_2[\mathbf{22}]\cdot 2\,CH_3OH$. The labelling of the donor groups (S and O) is arbitrary since all donor atoms are disordered. Hydrogen atoms have been omitted for clarity.

Synthesis of the dinuclear complexes $(PNP)_2[Ti_2(\mathbf{3})_2(\mu\text{-}OCH_3)_2]$ ($(PNP)_2[\mathbf{23}]$) and $(PNP)_4[Ti_2(\mathbf{3})_3]$ ($(PNP)_4[\mathbf{24}]$): Only the brown, double-stranded complex $Na_2[Ti_2(\mathbf{3})_2(\mu\text{-}OCH_3)_2]$ ($Na_2[\mathbf{23}]$) was obtained upon treatment of three equivalents of H_4-**3** with two equivalents of $[TiO(acac)_2]$ and Na_2CO_3 in methanol at 25 °C. Addition of two equivalents of (PNP)Cl (PNP^+ = bis(triphenylphosphoranylidene)ammonium) to a methanolic solution of $Na_2[\mathbf{23}]$ gave $(PNP)_2[Ti_2(\mathbf{3})_2(\mu\text{-}OCH_3)_2]$ ($(PNP)_2[\mathbf{23}]$) as a red solid, which was recrystallised from acetone/diethyl ether to yield analytically pure, crystalline $(PNP)_2[\mathbf{23}]$.

The complex dianion $[\mathbf{23}]^{2-}$ can exist as the same mixture of isomers as described for $[\mathbf{22}]^{2-}$ (Figure 1). However, the ^{1}H NMR spectrum of $(PNP)_2[\mathbf{23}]$ (Figure 5) shows only one set of signals for the aromatic protons of the ligand strands (four doublets and two triplets for the aromatic donor groups and two doublets of triplets and two doublets for the bridging phenylene group), thereby indicating that only one of the possible isomers is formed. This is corroborated by

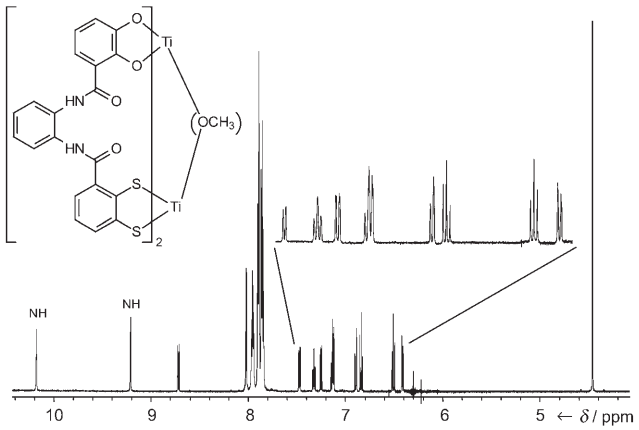


Figure 5. ^{1}H NMR spectrum of $(PNP)_2[\mathbf{23}]$ (in $[D_7]$DMF).

the observation of only two amide NH resonances at $\delta =$ 10.19 and 9.30 ppm. These resonances are shifted downfield to a different extent ($\Delta\delta = 0.31$ and 1.11 ppm) compared to the free ligand H_4-**3** (NH resonances at $\delta = 10.50$ and 10.41 ppm). We take this difference as an indication that only one NH proton of each ligand strand is engaged in a strong N–H···X (X = O, S) hydrogen bond. Owing to the differences in electronegativity and local charges at the donor atoms, it is reasonable to assume that N–H···O hydrogen bonds have been formed to the catecholato oxygen atoms.[17]

The NMR spectra of $(PNP)_2[\mathbf{23}]$ are consistent with both a parallel and an antiparallel orientation of the ligand strands. We therefore attempted to determine the molecular structure of $(PNP)_2[\mathbf{23}]$. Single crystals of $(PNP)_2[\mathbf{23}]$ suitable for an X-ray diffraction analysis were grown by slow diffusion of diethyl ether into a solution of $(PNP)_2[\mathbf{23}]$ in acetone. $(PNP)_2[\mathbf{23}]$ crystallises in the triclinic space group $P\bar{1}$ with $Z = 1$. The molecular structure of the dianion $[\mathbf{23}]^{2-}$ is depicted in Figure 6. The ligand strands in $[\mathbf{23}]^{2-}$ are oriented in a parallel fashion. One titanium atom (Ti2) is coordinated by six oxygen atoms in a distorted octahedral fashion, whereas the other titanium atom (Ti1) is coordinated by two oxygen atoms and four sulfur atoms, also in a distorted octahedral fashion, with the oxygen atoms in a *cis* arrangement.

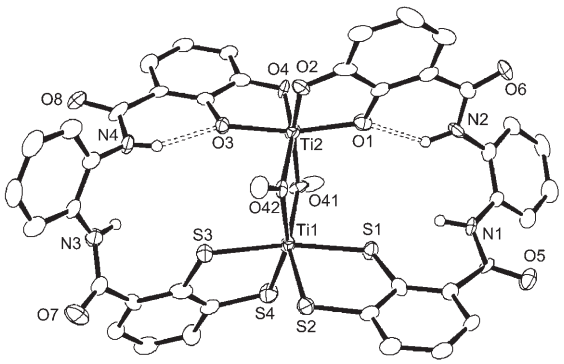


Figure 6. ORTEP plot of the anion $[\mathbf{23}]^{2-}$ with the amide hydrogen atoms shown at calculated positions. The dotted lines indicate hydrogen bonds.

The two titanium atoms and the methoxy ligands form the central $[Ti_2(\mu\text{-}OCH_3)_2]$ ring with a Ti···Ti separation of 3.180(2) Å (Table 1), which is similar to the value found in $[\mathbf{22}]^{2-}$ and in other complexes with a similar structure.[7a,16]

Table 1. Selected bond lengths [Å] and angles [°] in $(PNP)_2[\mathbf{23}]$.

Parameter		Parameter	
Ti1···Ti2	3.180(2)		
Ti1–S1	2.381(2)	Ti1–O42	2.009(5)
Ti1–S2	2.364(3)	Ti2–O41	2.008(5)
Ti1–S3	2.377(2)	Ti2–O42	1.996(5)
Ti1–S4	2.422(3)	S1-Ti1-S2	81.37(8)
Ti2–O1	1.990(5)	S3-Ti1-S4	81.87(8)
Ti2–O2	1.929(5)	O41-Ti1-O42	75.0(2)
Ti2–O3	1.975(5)	O1-Ti2-O2	79.8(2)
Ti2–O4	1.921(6)	O3-Ti2-O4	79.9(2)
Ti1–O41	2.010(5)	O41-Ti2-O42	75.3(2)

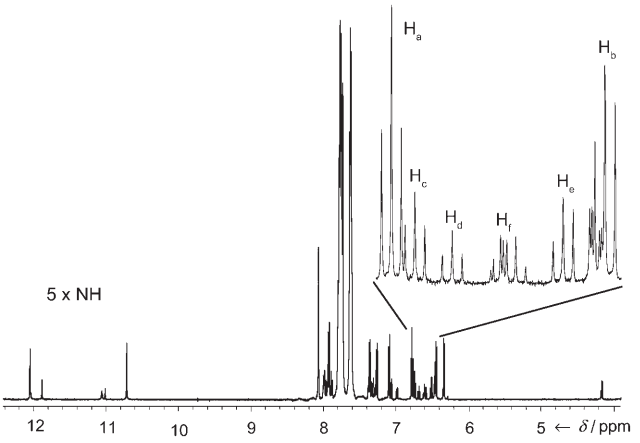


Figure 7. ^{1}H NMR spectrum of $(PNP)_4[\mathbf{24}]$ (in $[D_7]$DMF).

Strong N–H···O hydrogen bonds are formed in the solid state, as indicated by the ^{1}H NMR spectrum. This leads to nearly planar N–H···O–C–C–C rings and short, non-bonding N···O distances (N2···O1 2.779(8) and N4···O3 2.731(8) Å). Partly due to these strong N–H···O hydrogen bonds, the Ti–O bonds to the oxygen donors in the *ortho* position to the amide group are elongated (Ti2–O1 1.990(5) and Ti2–O3 1.975(5) Å), while the bonds to the oxygen atoms in the *meta* position are shorter (Ti2–O2 1.929(5) and Ti2–O4 1.921(6) Å). Contrary to this, the benzene-*o*-dithiolato amide subunits are not planar and exhibit long intramolecular N···S separations (N1···S1 2.948(6) and N3···S3 3.106(7) Å), which are indicative of weak or no N–H···S hydrogen bonds.

The reaction of three equivalents of H_4-**3** with two equivalents of $[TiO(acac)_2]$ and Na_2CO_3 in methanol at an elevated temperature of 50 °C initially leads to the formation of the double-stranded complex $Na_2[Ti_2(\mathbf{3})_2(\mu\text{-}OCH_3)_2]$ ($Na_2[\mathbf{23}]$). This double-stranded complex is quantitatively converted into the triple-stranded helicate $Na_4[Ti_2(\mathbf{3})_3]$ ($Na_4[\mathbf{24}]$) within 12 h at 50 °C. We assume that complex $Na_4[\mathbf{24}]$ is formed by a reaction between $Na_2[\mathbf{23}]$ and the deprotonated ligand $\mathbf{3}^{4-}$. This suggestion is corroborated by the observation that $Na_2[\mathbf{23}]$ does not form the triple-stranded helicate $Na_4[\mathbf{24}]$ at an elevated temperature in the absence of $\mathbf{3}^{4-}$.

The salt $(PNP)_4[Ti_2(\mathbf{3})_3]$ ($(PNP)_4[\mathbf{24}]$) was isolated as a red precipitate after addition of four equivalents of (PNP)Cl to a methanolic solution of $Na_4[\mathbf{24}]$. The ^{1}H NMR spectrum of $(PNP)_4[\mathbf{24}]$ shows more than one set of signals for the ligand strands, thus indicating that a mixture of isomers is present in solution (Figure 7). Due to an overlap of the signals, not all peaks in the ^{1}H NMR spectrum can be assigned unambiguously. However, six triplets are observed between $\delta =$ 6.73 and 6.39 ppm, which can be assigned to the protons H_a–H_f that are attached in the *meta* positions of the benzene-*o*-dithiolato and catecholato rings (Figure 8). This observation suggests that at least two isomers of $[\mathbf{24}]^{4-}$ are formed, namely the complex anions with a parallel and the one with an antiparallel orientation of the ligand strands.

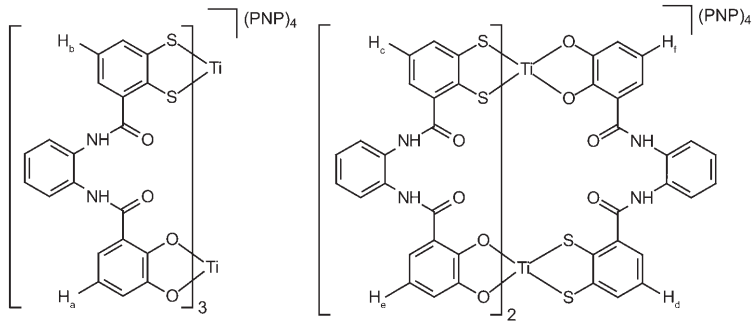


Figure 8. Possible regioisomers of the anion $[\mathbf{24}]^{4-}$.

Only five of the six expected signals for the amide protons (Figure 7, assuming the presence of anions $[\mathbf{24}]^{4-}$ with parallel and antiparallel orientations of the ligand strands; see Figure 8) are observed between $\delta = 12.03$ and 10.70 ppm. All signals for the amide protons are shifted downfield relative to those of the free ligand H_4-**3**, although to a different extent ($\Delta\delta = 0.19$–1.52 ppm). We therefore assume that strong N–H···O and weak N–H···S hydrogen bonds exist in the complex anion $[\mathbf{24}]^{4-}$ similar to those in the complex anion $[\mathbf{23}]^{2-}$.

An evaluation of the signal intensities shows that the triple-stranded helicate with a parallel orientation of the ligand strands is the major product (65 %), while the helicate with the antiparallel orientation is obtained as the minor product (35 %). We assume that the elevated reaction temperature employed for the preparation of $(PNP)_4[\mathbf{24}]$ is

responsible for the formation of the two isomeric complex anions $[\mathbf{24}]^{4-}$.

Synthesis of the triple-stranded helicates $Na(PNP)_3[Ti_2(\mathbf{1})_3]$ ($Na(PNP)_3[\mathbf{25}]$) and $Na(PNP)_3[Ti_2(\mathbf{4})_3]$ ($Na(PNP)_3[\mathbf{26}]$): Ligands H_4-**1** and H_4-**4** exclusively form dinuclear, triple-stranded helicates $Na_4[Ti_2(\mathbf{1})_3]$ ($Na_4[\mathbf{25}]$) and $Na_4[Ti_2(\mathbf{4})_3]$ ($Na_4[\mathbf{26}]$) when treated with $[TiO(acac)_2]$ in a 3:2 stoichiometry in the presence of Na_2CO_3. Attempts to obtain a dinuclear double-stranded complex $Na_2[Ti_2(\mathbf{1})_2(\mu\text{-}OCH_3)_2]$ related to $Na_4[\mathbf{22}]$ failed, even though H_4-**1** and H_4-**2** possess similar ligand backbones. Surprisingly, only three of the four sodium cations in $Na_4[\mathbf{25}]$ and $Na_4[\mathbf{26}]$ can be exchanged for PNP^+ cations upon addition of up to 10 equivalents of (PNP)Cl to methanolic solutions of $Na_4[\mathbf{25}]$ and $Na_4[\mathbf{26}]$. Compounds $Na(PNP)_3[\mathbf{25}]$ and $Na(PNP)_3[\mathbf{26}]$ were obtained as analytically pure red powders after recrystallisation from methanol/diethyl ether.

The ^1H NMR spectrum of $Na(PNP)_3[\mathbf{25}]$ shows only one set of signals for the ligand strands, which is indicative of the formation of only one geometrical isomer of $[\mathbf{25}]^{4-}$ with a parallel orientation of the ligand strands in solution. The aromatic protons of the benzene-*o*-dithiolato and catecholato groups appear as one triplet ($\delta = 6.65$ (H_g) and 6.32 (H_c) ppm) and two doublets ($\delta = 7.08$ (H_f), 6.98 (H_h) and $\delta = 7.15$ (H_b), 6.21 ppm (H_d)) for each ring (Figure 9). The triplet at $\delta = 9.80$ ppm was assigned to the catechoyl amide NH proton (H_a) based on the observed coupling with the neighbouring CH_2 group of the bridging unit. The downfield shift ($\Delta\delta = 0.70$ ppm) of this NH signal (Figure 9, bottom) relative to the free ligand H_4-**1** (Figure 9, top) indicates the formation of a strong N–H···O hydrogen bond in $[\mathbf{25}]^{4-}$. Contrary to this, the resonance for the amide proton of the benzene-*o*-dithiolato amide subunit in $[\mathbf{25}]^{4-}$ (H_e at $\delta =$ 8.14 ppm) is shifted slightly to high field ($\Delta\delta = -0.11$ ppm) compared to the free ligand. This indicates that no or only weak N–H···S hydrogen bonds exist in $[\mathbf{25}]^{4-}$. The NMR spectroscopic data indicate the presence of the parallel regioisomer and only one pair of stereoisomers in solution. However, they do not allow the determination of which pair of stereoisomers (Λ,Δ/Δ,Λ or Λ,Λ/Δ,Δ complexes) is present.

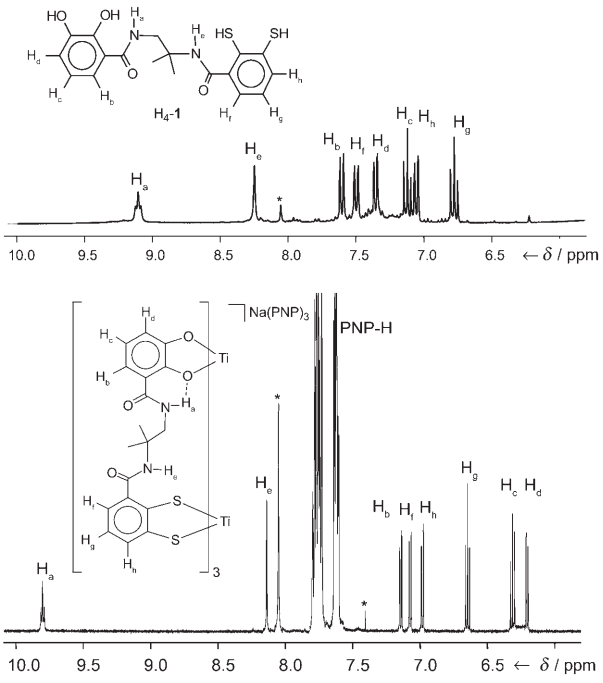


Figure 9. ^1H NMR spectra (in $[D_7]$DMF, * = DMF resonances) of H_4-**1** (top) and $Na(PNP)_3[\mathbf{25}]$ (bottom).

Single crystals of $Na(PNP)_3[\mathbf{25}]\cdot CH_3OH\cdot H_2O\cdot Et_2O$ suitable for an X-ray diffraction analysis were grown by slow diffusion of diethyl ether into a solution of $Na(PNP)_3[\mathbf{25}]$ in wet methanol. The complex crystallises in the triclinic space group $P\bar{1}$ with $Z = 1$. The molecular structure of the anion $[\mathbf{25}]^{4-}$ is depicted in Figure 10. It confirms the parallel orientation of the ligand strands that was concluded from the NMR spectroscopic data. Each of the titanium atoms is coordinated by six identical donor atoms (O or S) in a distorted octahedral fashion. The Ti–O bond lengths (Table 2) fall in the range reported for other Ti^{IV} tris(catecholato) complexes.[23] The Ti–S bond lengths vary only slightly and are comparable to bond lengths reported for tris(*o*-benzenedithiolato) complexes of Ti^{IV}.[24] A helical twist of 65.6° has been calculated. Both titanium atoms in the studied crystal of $Na(PNP)_3[\mathbf{25}]$ assume the same configuration, namely Λ. Since it crystallises in the acentric space group $P\bar{1}$, the Δ,Δ stereoisomer must also have formed during the reaction. A similar spontaneous resolution of stereoisomers upon crystallisation was first described for triple-stranded Ni^{II} complexes with oligobipyridine ligands.[25] At ambient temperature we observed the formation of only one pair of helical stereoisomers. However, the formation of *meso* helicates of the Λ,Δ and Δ,Λ type might be possible by a dynamic process, for example at elevated temperature.

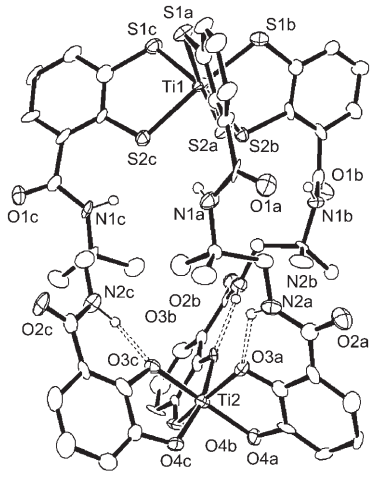


Figure 10. ORTEP diagram of the anion $[\mathbf{25}]^{4-}$ with amide hydrogen atoms at calculated positions. The dotted lines indicate hydrogen bonds.

Table 2. Selected bond lengths [Å] and angles [°] in complexes $Na(PNP)_3$[**25**] and $Na_{1.5}(PNP)_{6.5}$[**26**]$_2$.

	$Na(PNP)_3$[**25**]	$Na_{1.5}(PNP)_{6.5}$[**26**]$_2$[a]
Ti1–Ti2	9.795(2)	12.460/12.514
Ti1–S1a(S12)	2.392(3)	2.369(5)/2.390(4)
Ti1–S1b	2.381(3)	
Ti1–S1c	2.387(3)	
Ti1–S2a(S11)	2.416(3)	2.427(5)/2.427(4)
Ti1–S2b	2.436(3)	
Ti1–S2c	2.430(3)	
Ti2–O3a(O34)	1.992(6)	2.007(9)/1.988(10)
Ti2–O3b	2.010(6)	
Ti2–O3c	1.977(6)	
Ti2–O4a(O33)	1.941(6)	2.016(10)/1.960(11)
Ti2–O4b	1.915(6)	
Ti2–O4c	1.904(6)	
S1a(S11)-Ti1-S2a(S12)	81.94(9)	81.83(15)/81.61(12)
S1b-Ti1-S2b	81.64(9)	
S1c-Ti1-S2c	81.68(9)	
O3a(O33)-Ti2-O4a(O34)	79.8(2)	80.4(4)/79.7(4)
O3b-Ti2-O4b	78.9(2)	
O3c-Ti2-O4c	80.0(3)	

[a] The asymmetric unit contains 1/3 of the anion $\{[\mathbf{26}]^{4-}\text{-}Na^{+}\text{-}[\mathbf{26}]^{4-}\}^{7-}$; the titanium and sodium atoms reside on special positions on a threefold axis (Wyckoff position *c*, site symmetry 3).

As was seen in the ^{1}H NMR spectrum for solutions of $Na(PNP)_3$[**25**], strong N–H···O hydrogen bonds also exist in the solid state. This leads to nearly planar N–H···O–C–C–C rings and short intramolecular nonbonding N···O distances (2.664(10)–2.673(10) Å). In contrast, the benzene-*o*-dithiolato amide subunits exhibit non-planar N–H···S–C–C–C rings (Figure 10) and longer intramolecular nonbonding N···S distances (3.051(8)–3.193(7) Å), which indicates that only weak or no N–H···S hydrogen bonds exist in the solid state.

The Ti–O bonds to the oxygen donors in the *ortho* position to the amide function are slightly longer (1.977(6)–2.010(6) Å) than those to the oxygen donors in the *meta* position (1.904(6)–1.941(6) Å, Table 2). A similar effect is observed for the benzene-*o*-dithiolato groups, where the Ti–S bonds to the sulfur donors in the *ortho* position are slightly longer (2.416(3)–2.436(3) Å) than those to the sulfur donor atoms in the *meta* position to the amide function (2.381(3)–2.392(3) Å). While the effect is smaller for the Ti–S bonds than for the Ti–O bonds, it cannot be attributed exclusively to the existence of intramolecular hydrogen bonds, as such interactions only exist in the catechoyl amide part of the complex anion.

The unit cell contains one $[\mathbf{25}]^{4-}$ ion, three PNP cations, one sodium cation and one molecule each of water, methanol and (disordered) diethyl ether. The PNP cations maintain no remarkable contacts with the anion whereas the Na^+ cation acts as a bridge between the $[\mathbf{25}]^{4-}$ anions by coordinating to the amide carbonyl functions of two different anions, which leads to the formation of infinite chains in the crystal lattice (Figure 11). The Na^+ ions complete their coordination sphere by coordinating to one molecule each of methanol and water.

We can only speculate about the driving force for the formation of the triple-stranded helical complex anion $[\mathbf{25}]^{4-}$ containing parallel oriented ligand strands. With the related directional ligand containing catechol/aminophenol donor groups reported by Albrecht et al., only the antiparallel ligand orientation, which leads to a minimal charge separation in the complex, was observed for homobinuclear complexes.[14] The directional ligand H_4-**1** was expected to behave similarly. However, H_4-**1** is a directional ligand with regards to both the donor groups and the spacer between them. Upon formation of the triple-stranded helicate $[\mathbf{25}]^{4-}$ a distorted $\{TiS_6\}$ octahedron and a smaller $\{TiO_6\}$ octahedron are obtained. It is reasonable to expect that the sterically more demanding part of the unsymmetrical -$C(Me)_2$-CH_2- spacer is oriented towards the larger $\{TiS_6\}$ octahedron, thereby causing the parallel orientation of the ligand strands. This orientation allows the formation of three stable intramolecular N–H···O hydrogen bonds and of three almost planar N–H···O–C–C–C(O) rings within the catechoyl amide groups at the $\{TiO_6\}$ octahedron (Figure 10). This type of intramolecular hydrogen bond has been observed for other helicates with amide- bridged catecholato donor groups[6c,7b] and for other catechoyl amide complexes,[26] and has often been shown to determine the molecular structure.[27] Similarly strong N–H···S hydrogen bonds were not observed in $[\mathbf{25}]^{4-}$, and the benzenedithiolato groups are not coplanar with the attached amide groups. We therefore propose a structure-determining influence of the unsymmetrical -$C(Me)_2$-CH_2- spacer on the formation of the parallel regioisomer of $[\mathbf{25}]^{4-}$. This postulate is corroborated by the observation that ligand H_4-**2**, which contains a symmetrical CH_2-CH_2 spacer, forms, among others, the dinuclear Ti^{IV} complex $[Ti_2(\mathbf{2})_2(OMe)_2]^{2-}$, which has an antiparallel orientation of the ligand strands.

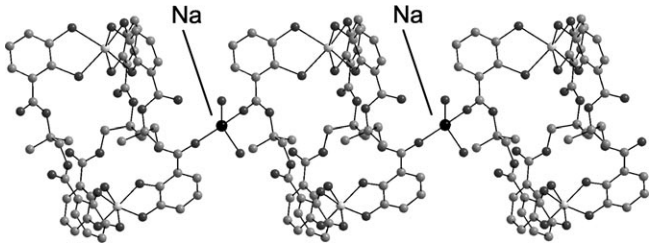


Figure 11. Part of the crystal structure of $Na(PNP)_3$[**25**]·H_3OH·Et_2O·H_2O. The PNP^+ ions and the disordered diethyl ether molecule have been omitted. Only the oxygen donor atoms of the water and methanol molecules coordinated to the bridging sodium cation are depicted.

The reaction of three equivalents of H_4-**4**, two equivalents of $[TiO(acac)_2]$ and Na_2CO_3 in methanol at room temperature under argon yields a deep red solution of $Na_4[Ti_2(\mathbf{4})_3]$ (Na_4[**26**]). As was observed with $Na(PNP)_3$[**25**], only three of the four sodium cations can be substituted with PNP^+ cations, even when a large excess of (PNP)Cl (up to 10 equiv) is added to a methanolic solution of Na_4(**26**). The ^{1}H NMR spectrum of $Na(PNP)_3$[**26**] consists of only one set of signals, which is in accordance with the presence of only one regioisomer with a parallel orientation of the ligand strands. Two signals are been observed for the amide protons, at $\delta = 12.01$ and 10.68 ppm. The strong downfield shift

for the protons of the catechoyl amide group in $[\mathbf{26}]^{4-}$ ($\Delta\delta =$ 1.5 ppm) relative to the signal in the free ligand H_4-**4** is caused by the formation of strong N–H···O hydrogen bonds. The signal for the benzene-*o*-dithiolato-bound amide protons is shifted only slightly downfield ($\Delta\delta = 0.17$ ppm), thus indicating that no, or only weak, N–H···S hydrogen bonds exist in the anion $[\mathbf{26}]^{4-}$.

Attempts to crystallise $Na(PNP)_3[\mathbf{26}]$ by vapour diffusion of diethyl ether into a solution of $Na(PNP)_3[\mathbf{26}]$ in DMF led to the formation of single crystals of $Na_{1.5}(PNP)_{6.5}[\mathbf{26}]_2 \cdot 3\,DMF$ suitable for an X-ray analysis. The complex crystallises in the hexagonal space group $R\bar{3}c$ ($Z = 12$). The titanium atoms and the sodium atoms of the $\{[\mathbf{26}]\text{-Na-}[\mathbf{26}]\}^{7-}$ unit reside on a threefold crystallographic axis. Nearly identical structural parameters are observed for the two $[\mathbf{26}]^{4-}$ anions in each $\{[\mathbf{26}]\text{-Na-}[\mathbf{26}]\}^{7-}$ unit (Table 2), including identical configurations at all titanium centres. The crystal structure of one of the $[\mathbf{26}]^{4-}$ anions with a Λ,Λ configuration is depicted in Figure 12 and confirms the parallel orientation of the ligand strands. Both titanium atoms are coordinated in a slightly distorted octahedral fashion by six identical donor atoms (O or S).

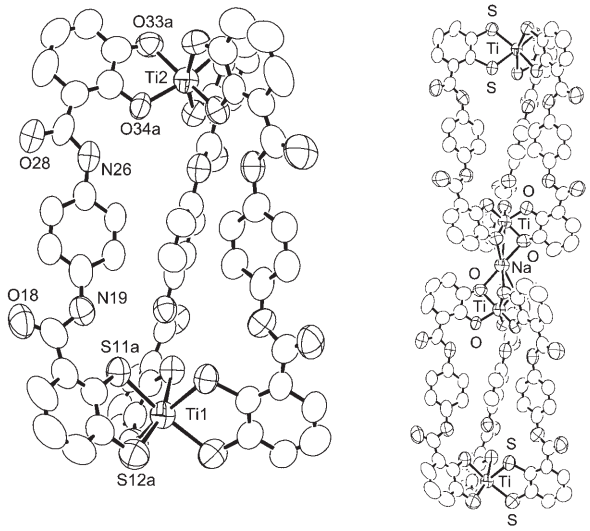


Figure 12. ORTEP diagram of one $[\mathbf{26}]^{4-}$ anion (left) and the aggregate $\{[\mathbf{26}]\text{-Na-}[\mathbf{26}]\}^{7-}$ (right). The asymmetric unit contains 1/3 of the anion $\{[\mathbf{26}]^{4-}\text{-}Na^{+}\text{-}[\mathbf{26}]^{4-}\}^{7-}$; the titanium and sodium atoms reside on a special position on a threefold axis.

Although nearly planar catechoyl amide subunits, and therefore strong N–H···O hydrogen bonds (N–O nonbonding distances of 2.68(2)–2.73(2) Å), are formed in the solid state, the Ti–O bonds to the two different oxygen donor atoms are nearly uniform (2.007(9) and 2.016(10)/1.988(10) and 1.960(11) Å, Table 2). We assume that the coordination of the sodium cation to the three oxygen donor atoms in the *meta* position to the amide group has a similar effect as the N–H···O hydrogen bonds and leads to a similar elongation of the Ti–O bonds.

Bridging of related triple-stranded helicates containing dicatecholato ligands by alkali cations, which leads to linear polymeric chains, has been described.[3b] The formation of the linear polymeric chain $Na^{+}\text{-}[\mathbf{26}]^{4-}\text{-}Na^{+}\text{-}[\mathbf{26}]^{4-}\text{-}Na^{+}$ is, however, not possible, since the coordination of the soft sulfur donors to the hard sodium cations is unfavourable.

Conclusion

We have reported the synthesis of a series of mixed benzene-*o*-dithiol/catechol ligands and their coordination chemistry with titanium(IV). Dinuclear, triple-stranded helicates $[Ti_2(\mathbf{L})_3]^{4-}$ and dinuclear, double-stranded complexes $[Ti_2(\mathbf{L})_2(\mu\text{-}OCH_3)_2]^{2-}$ are formed depending on the ligand backbone and the reaction conditions. The directionality of the ligand strands in $\mathbf{2}^{4-}$ leads to the formation of up to three of four possible isomers/pairs of stereoisomers in solution. For most of the complexes that have been investigated, a parallel orientation of the ligand strands is observed. We are currently investigating the preparation and properties of heterodinuclear complexes with mixed benzene-*o*-dithiolato/catecholato ligands. In particular, the formation of triple-stranded helicates containing both $\{Ti(catecholato)_3\}^{2-}$ and $\{M(bdt)_3\}^{n-}$ units is of interest since complexes of the type $[M(bdt)_3]^{n-}$ (M = Mo, W, $n = 0$, 1, 2)[18,19] can adopt a trigonal-prismatic ($n = 0$) or octahedral ($n = 1$) coordination geometry. Redox reactions at heterodinuclear (Mo,W/Ti), triple-stranded helicates could be used to change the coordination geometry at one of the metal centres (MoS_6, WS_6), while the geometry at the other metal centre (TiO_6) remains unchanged. This would, in principle, allow the switching on or off of the helicity of the triple-stranded, heterodinuclear helicate by a redox reaction.

Experimental Section

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 at 25 °C with a Bruker AC 200 (200 MHz), Bruker AMX 400 (400 MHz) or Varian Inova (600 MHz) spectrometer and are reported relative to TMS as an internal standard or to the solvent signal. IR spectra were recorded with a Bruker Vector 22 IR spectrometer. Mass spectra were measured with a Varian MAT 212 (EI), a Micromass Quattro LC-Z (ESI) or a Bruker Reflex IV (MALDI) spectrometer. Elemental analyses were performed with a Vario EL III CHNS analyzer. Commercially available $[TiO(acac)_2]$ (Aldrich) was used without further purification. 2,3-Di(isopropylmercapto)benzoic acid chloride[10,11] and 2,3-di(benzyloxy)benzoic acid chloride[22] were prepared as described previously.

1,2-Diamino-*N*-(*tert*-butyloxycarbonyl)ethane (6): A solution of di-*tert*-butyl dicarbonate (3.84 g, 17.6 mmol) in chloroform (50 mL) was added at 0 °C to a solution of ethylenediamine (6 mL, 88 mmol) in chloroform (400 mL) and the mixture was stirred for 12 h at ambient temperature. The solvent was removed in vacuo and the remaining solid was dissolved in ethyl acetate. The organic phase was washed with NaCl solution (10 mL, 35 %), dried with Na_2SO_4 and the solvent removed in vacuo. Compound **6** was obtained as a colourless oil after distillation in vacuo. Yield: 2.4 g (15.0 mmol, 85 %). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.28$ (s,

1H; C(O)NH), 3.02 (q, ^3J=6.1 Hz, 2H; NHCH_2), 2.66 (t, ^3J=6.1 Hz, 2H; NH_2CH_2), 1.31 (s, 9H; CH_3), 1.12 ppm (s, 2H; NH_2); ^{13}C NMR (50 MHz, $CDCl_3$): δ=156.1 (C(O)NH), 78.7 (O*C*(CH_3)$_3$), 43.2 ($NHCH_2$), 41.6 (NH_2CH_2), 28.2 ppm (CH_3); elemental analysis calcd (%) for $C_7H_{16}N_2O_2$: C 52.48, H 10.07, N 17.48; found: C 52.24, H 10.12, N 17.32.

1,2-Diamino-*N*-(*tert*-butyloxycarbonyl)-1,1′-dimethylethane (10): Compound **10** was prepared as described for **6** from di-*tert*-butyl dicarbonate (3.84 g, 17.6 mmol) and (1,1′-dimethylethylenediamine (7.75 g, 88 mmol). Yield: 2.5 g (13.5 mmol, 77%) of a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ=5.12 (br.s, 1H; C(O)NH), 3.96 (s, 1H; C(O)NH-C*H*H), 2.94 (s, 1H; C(O)NH-C*H*H), 1.77 (s, 2H; NH_2), 1.38 (s, 9H; CH_3), 1.04 ppm (s, 6H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ=156.8 (C(O)NH), 79.4 (O*C*(CH_3)$_3$), 52.3 (N*C*(CH_3)$_2$$CH_2$), 50.8 (NC($CH_3$)$_2$*C*$H_2$), 28.9 (OC(*C*$H_3$)$_3$), 28.3 ppm (NC(*C*$H_3$)$_2$$CH_2$); elemental analysis calcd (%) for $C_9H_{20}N_2O_2$: C 57.42, H 10.71, N 14.88; found: C 57.37, H 10.51, N 14.34.

1,2-Diamino-*N*-(*tert*-butyloxycarbonyl)benzene (14): 1,2-Diaminobenzene (2.5 g, 25 mmol) and Boc-ON (6.15 g, 25 mmol) were dissolved in DMF (50 mL) and heated to 55°C for 3 h. The solvent was removed in vacuo and the residue dissolved in toluene (60 mL). The organic layer was washed with aqueous NaOH (10%, 2×50 mL) and NaCl (10%, 2× 50 mL) and dried with $MgSO_4$. Recrystallisation from chloroform/hexane gave a colourless powder. Yield: 3.0 g (15.8 mmol, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.43 (dd, 1H; Ar-H), 7.15 (td, 1H; Ar-H), 6.93 (td, 1H; Ar-H), 6.89 (dd, 1H; Ar-H), 6.61 (s, 1H; C(O)NH), 3.88 (s, 2H; NH_2), 1.69 ppm (s, 9H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=153.8 (C(O)NH), 139.9, 125.9, 124.7, 124.6, 119.3, 117.3 (Ar-C), 80.3 (O*C*(CH_3)$_3$), 28.2 ppm (OC(*C*H_3)$_3$); MS (70 eV): *m*/*z* (%) 208 (53) [M^+], 152 (99) [M^+−*t*Bu], 135 (38) [M^+−O*t*Bu], 108 (100) [M^+−Boc]; elemental analysis calcd (%) for $C_{11}H_{16}N_2O_2$: C 63.44, H 7.74, N 13.45; found: C 63.30, H 7.61, N 13.34.

1,4-Diamino-*N*-(*tert*-butyloxycarbonyl)benzene (18): Compound **18** was prepared as described for **14** from 1,4-diaminobenzene (2.5 g, 25 mmol) and Boc-ON (6.15 g, 25 mmol). Yield: 4.6 g (22.3 mmol, 89%) of a colourless powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.36 (d, 2H; Ar-H), 6.86 (br.d, 2H; Ar-H), 6.70 (br.s, 1H; C(O)NH), 3.73 (s, 2H; NH_2), 1.76 ppm (s, 9H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=153.3 (C(O)NH), 142.4, 129.6, 121.0, 115.4 (Ar-C), 79.8 (O*C*(CH_3)$_3$), 28.3 ppm (C(*C*H_3)$_3$); MS (70 eV): *m*/*z* (%) 208 (26) [M^+], 152 (100) [M^+−*t*Bu], 135 (8) [M^+ −O*t*Bu], 108 (71) [M^+−Boc]; elemental analysis calcd (%) for $C_{11}H_{16}N_2O_2$: C 63.44, H 7.74, N 13.45; found: C 63.38, H 7.58, N 13.16.

1-(*tert*-Butyloxycarbamido)-2-[2,3-di(isopropylmercapto)benzamido]-ethane (7): A solution of 2,3-di(isopropylmercapto)benzoic acid chloride (**5**; 1.27 g, 4.4 mmol) in THF (10 mL) was added to a solution of NEt_3 (700 μL, 4.84 mmol) and *N*-(*tert*-butyloxycarbonyl)-1,2-diaminoethane (**6**; 700 mg, 4.4 mmol) in THF (50 mL). The solution was stirred for 12 h and the NEt_3·HCl formed was filtered off. The solvent was removed in vacuo and the residue was washed with water and dichloromethane to give **7** as a white powder. Yield: 1.55 g (3.78 mmol, 86%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.24 (m, 3H; Ar-H), 6.82 (s, 1H; NH), 5.22 (s, 1H; NH), 3.41 (m, 6H; S-C*H*(CH_3)$_2$ and CH_2-C*H*$_2$), 1.38 (s, 9H; OC(C*H*$_3$)$_3$), 1.34 (d, 6H; CH(C*H*$_3$)$_2$), 1.17 ppm (d, 6H; CH(C*H*$_3$)$_2$); ^{13}C NMR (50 MHz, $CDCl_3$): δ=169.2, 156.2 (NHC(O)), 145.7, 143.5, 128.9, 128.5, 127.4, 124.5 (Ar-C), 79.3 (O*C*(CH_3)$_3$), 40.4 (SCH), 40.2 (CH_2), 39.6 (CH_2), 35.9 (SCH), 28.3 (OC(*C*H_3)$_3$), 23.1 (CH(*C*H_3)$_2$), 22.5 ppm (CH(*C*H_3)$_2$); elemental analysis calcd (%) for $C_{20}H_{32}N_2O_3S_2$: C 58.22, H 7.82, N 6.79; found: C 58.16, H 8.01, N 6.56.

1-(*tert*-Butyloxycarbamido)-2-[2,3-di(isopropylmercapto)benzamido]-2,2′-dimethylethane (11): Compound **11** was prepared as described for **7** from a solution of **5** (1.27 g, 4.4 mmol) in THF (10 mL), NEt_3 (700 μL, 4.84 mmol) and *N*-(*tert*-butyloxycarbonyl)-1,1′-dimethyl-1,2-diaminoethane (**10**; 828 mg, 4.4 mmol) in THF (50 mL). Yield: 1.56 g (3.56 mmol, 81%) of a colourless powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.37–7.48 (m, 3H; Ar-H), 6.31 (br.s, 1H; N*H*C(CH_3)$_2$), 5.79 (br.t, 1H; N*H*CH_2), 3.60–3.74 (m, 4H; SC*H*(CH_3)$_2$, NHC*H*$_2$), 1.60 (s, 9H; OC(CH_3)$_3$), 1.55 (d, 6H; CH(C*H*$_3$)$_2$), 1.55 (s, 6H; C(C*H*$_3$)$_2$$CH_2$), 1.40 ppm (d, 6H; CH(C*H*$_3$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=169.0, 157.1 (CO), 146.1, 145.2, 129.4, 128.8, 127.7, 124.5 (Ar-C), 79.5 (O*C*(CH_3)$_3$), 59.3 (*C*(CH_3)$_2$$CH_2$), 56.0 ($CH_2$), 40.4 (S*C*H), 36.4 (S*C*H), 28.8 (OC(*C*H_3)$_3$), 25.4 (C-(CH_3)$_2$$CH_2$), 23.1 (CH(*C*$H_3$)$_2$), 22.4 ppm (CH(*C*$H_3$)$_2$); elemental analysis calcd (%) for $C_{22}H_{36}N_2O_3S_2$: C 59.97, H 8.23, N 6.36; found: C 58.95, H 8.28, N 6.29.

1-(*tert*-Butylcarbamido)-2-[2,3-di(isopropylmercapto)benzamido]benzene (15): A solution of **5** (1.07 g, 3.7 mmol) in THF (10 mL) was added to a solution of NEt_3 (560 μL, 3.85 mmol) and *N*-(*tert*-butyloxycarbonyl)-1,2-diaminobenzene (**14**; 772 mg, 3.7 mmol) in THF (30 mL). The solution was stirred for 12 h at ambient temperature and NEt_3·HCl was then filtered off. The solvent was removed in vacuo and the solid obtained was washed with water and diethyl ether. Compound **15** was obtained as white powder. Yield: 1.48 g (3.21 mmol, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.58 (br.s, 1H; NH), 7.82 (d, 1H; Ar-H), 7.56–7.17 (m, 6H; Ar-H), 6.73 (s, 1H; NH), 3.66–3.52 (m, 2H; C*H*(CH_3)$_2$), 1.56 (s, 9H; OC-(C*H*$_3$)$_3$), 1.47 (d, 6H; CH(C*H*$_3$)$_2$), 1.31 ppm (d, 6H; CH(C*H*$_3$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=168.0, 154.0 (CO), 146.5, 143.3, 132.9, 131.7, 129.5, 128.7, 128.4, 127.4, 125.9, 125.7, 124.9, 123.9 (Ar-C), 81.0 (O*C*(CH_3)$_3$), 41.4 (SCH), 36.6 (SCH), 28.8 (C(*C*H_3)$_3$), 23.5 (CH(*C*H_3)$_2$), 23.1 ppm (CH(*C*H_3)$_2$); elemental analysis calcd (%) for $C_{24}H_{32}N_2O_3S_2$: C 62.58, H 7.00, N 6.08; found: C 62.60, H 6.95, N 6.06.

1-(*tert*-Butylcarbamido)-4-[2,3-di(isopropylmercapto)benzamido]benzene (19): Compound **19** was prepared as described for **15** from a solution of **5** (1.07 g, 3.7 mmol) in THF (10 mL), NEt_3 (560 μL, 3.85 mmol) and *N*-(*tert*-butyloxycarbonyl)-1,4-diaminobenzene (**18**; 772 mg, 3.7 mmol) in THF (30 mL). Yield: 1.54 g (3.34 mmol, 89%) of a colourless powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.85 (br.s, 1H; NH), 7.56–7.29 (m, 7H; Ar-H), 6.57 (br.s, 1H; NH), 3.45 (sept, 1H; C*H*(CH_3)$_2$), 3.37 (sept, 1H; C*H*(CH_3)$_2$), 1.47 (s, 9H; OC(CH_3)$_3$), 1.35 (d, 6H; CH(C*H*$_3$)$_2$), 1.16 ppm (d, 6H; CH(C*H*$_3$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=166.9, 153.3 (CO), 146.2, 142.5, 135.4, 133.7, 129.5, 128.9, 126.7, 121.1, 119.8 (Ar-C), 80.9 (O*C*(CH_3)$_3$), 41.7 (SCH), 36.6 (SCH), 28.7 (OC(*C*H_3)$_3$), 23.5 (CH(*C*H_3)$_2$), 23.0 ppm (CH(*C*H_3)$_2$); MS (70 eV): *m*/*z* (%) 460 (24) [M^+], 360 (42) [M^+−Boc], 317 (18) [M^+−Boc−*i*Pr], 253 (64) [M^+−NH(C_6H_4)NHBoc], 211 (67) [M^+−NH(C_6H_4)NHBoc−*i*Pr]$^+$, 152 (100); elemental analysis calcd (%) for $C_{24}H_{32}N_2O_3S_2$: C 62.58, H 7.00, N 6.08; found: C 62.59, H 6.90, N 5.96.

1-Amino-2-[2,3-di(isopropylmercapto)benzamido]ethane (8): A sample of compound **7** (1.55 g, 3.75 mmol) was dissolved in chloroform (15 mL) and trifluoroacetic acid (3 mL, 15.2 mmol) was added carefully. The solution was stirred for 24 h at ambient temperature and the solvent was removed in vacuo. Hydrochloric acid (20 mL, 5 M) was added and the aqueous phase was washed with diethyl ether (2×20 mL). NaOH was then added to the aqueous phase and this phase was extracted at pH 14 with dichloromethane (3×20 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed in vacuo to give **8**. Yield: 0.99 g (3.2 mmol, 84%) of a white powder. ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.25 (m, 3H; Ar-H), 6.89 (br.s, 1H; NH), 3.43 (sept, 2H; C*H*(CH_3)$_2$), 3.40 (q, 2H; C(O)NHC*H*$_2$), 2.86 (t, 2H; C*H*$_2$$NH_2$), 1.37 (s, 2H; NH_2), 1.33 (d, 6H; CH(C*H*$_3$)$_2$), 1.15 ppm (d, 6H; CH(C*H*$_3$)$_2$); ^{13}C NMR (50 MHz, $CDCl_3$): δ=168.9 (CO), 149.2, 145.5, 143.6, 128.7, 127.5, 124.7 (Ar-C), 42.8 (C(O)NH*C*H$_2$), 41.3 (NH_2CH_2), 40.4 (SCH), 36.0 (SCH), 22.9 (CH(*C*H_3)$_2$), 22.5 ppm (CH(*C*H_3)$_2$); elemental analysis calcd (%) for $C_{15}H_{24}N_2OS_2$: C 57.65, H 7.74, N 8.96; found: C 57.13, H 7.60, N 8.72.

1-Amino-2-[2,3-di(isopropylmercapto)benzamido]-2-(2,2′-dimethyl)-ethane (12): Compound **12** was prepared as described for **8** from **11** (1.67 g, 3.75 mmol) and trifluoroacetic acid (3 mL, 15.2 mmol). Yield 0.83 g (2.43 mmol, 64%) of a white powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.53–7.44 (m, 3H; Ar-H), 6.60 (br.s, 1H; NH), 3.78–3.65 (m, 2H; C*H*-(CH_3)$_2$), 3.13 (s, 2H; C*H*$_2$$NH_2$), 1.86 (s, 2H; NH_2), 1.62 (s, 6H; C-(C*H*$_3$)$_2$$CH_2$), 1.59 (d, 6H; CH(C*H*$_3$)$_2$), 1.44 ppm (d, 6H; CH(C*H*$_3$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=168.7 (CO), 146.0, 145.1, 129.3, 128.9, 127.5, 124.8 (Ar-C), 55.5 (*C*(CH_3)$_2$$CH_2$), 50.9 (C($CH_3$)$_2$*C*$H_2$), 40.8 (SCH), 36.3 (SCH), 25.1 (CH_3), 23.4 (CH(*C*H_3)$_2$), 23.1 ppm (CH(*C*H_3)$_2$); elemental analysis calcd (%) for $C_{17}H_{28}N_2OS_2$: C 59.96, H 8.29, N 8.23, S 18.83; found: C 59.67, H 8.09, N 8.09, S 18.44.

1-(Ammonium chlorido)-2-[2,3-di(isopropylmercapto)benzamido]benzene (16): Compound **15** (1.0 g, 2.17 mmol) was dissolved in chloroform (20 mL) and trifluoroacetic acid (1.67 mL, 21.7 mmol) was added dropwise. The solution was stirred for 24 h at ambient temperature and the

solvent was removed in vacuo. The residue was dissolved in hydrochloric acid (40 mL, 5 M) and diethyl ether was added dropwise. The precipitate was filtered off, washed with diethyl ether and dried in vacuo to give **16** as a colourless powder. Yield: 0.79 g (1.98 mmol, 91 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.67$ (s, 1H; NH), 7.55–7.41 (m, 7H; Ar-H), 4.86 (s, 3H; NH_2·HCl), 3.66–3.44 (m, 2H; C*H*(CH_3)$_2$), 1.34 (d, 6H; CH(CH_3)$_2$), 1.15 ppm (d, 6H; CH(CH_3)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 190.3 (CO), 177.6, 171.6, 147.6, 145.2, 133.3, 130.8, 130.4, 129.4, 127.4, 127.2, 125.9, 125.5 (Ar-C), 41.3 (SCH), 37.5 (SCH), 23.9 (CH(*C*H$_3$)$_2$), 23.6 ppm (CH(*C*H$_3$)$_2$); elemental analysis calcd (%) for $C_{19}H_{25}ClN_2OS_2$: C 57.48, H 6.35, N 7.06; found: C 57.41, H 6.21, N 6.99.

1-(Ammonium chlorido)-2-[2,3-di(isopropylmercapto)benzamido]benzene (20): Compound **20** was prepared as described for **16** from **19** (1.0 g, 2.17 mmol) and trifluoroacetic acid (1.67 mL, 21.7 mmol). Yield: 0.78 g (1.96 mmol, 90 %) of a colourless powder. ^{1}H NMR (300 MHz, CD_3OD): $\delta = 8.01$–7.96 (m, 2H; Ar-H), 7.63–7.53 (m, 4H; Ar-H), 7.39 (dd, 1H; Ar-H), 4.94 (br.s, 3H; NH_2 ·HCl), 3.76 (sept, 1H; C*H*(CH_3)$_2$), 3.65 (sept, 1H; C*H*(CH_3)$_2$), 1.51 (d, 6H; CH(CH_3)$_2$), 1.31 ppm (d, 6H; CH(CH_3)$_2$); ^{13}C NMR (75 MHz, CD_3OD): $\delta = 177.2$ (CO), 147.0, 145.8, 143.5, 140.7, 130.8, 130.2, 129.5, 127.4, 124.7, 122.5 (Ar-C), 40.7 (SCH), 36.9 (SCH), 23.6 (CH(*C*H$_3$)$_2$), 23.1 ppm (CH(*C*H$_3$)$_2$); elemental analysis calcd (%) for $C_{19}H_{25}N_2ClOS_2$: C 57.48, H 6.35, N 7.06; found: C 57.50, H 6.23, N 6.91.

1-[2,3-Di(benzyloxy)benzamido]-2-[2,3-di(isopropylmercapto)benzamido]ethane (9): A sample of 2,3-di(benzyloxy)benzoic acid chloride (457 mg, 1.37 mmol) was dissolved in THF (20 mL) and this solution was added dropwise to a solution of NEt_3 (207 μL, 1.51 mmol) and compound **8** (430 mg, 1.37 mmol) in THF (30 mL). The reaction mixture was stirred for 12 h at ambient temperature and the NEt_3·HCl formed was then filtered off. The solvent was removed in vacuo and the crude product was purified by column chromatography (SiO_2; CH_2Cl_2 then ethyl acetate) to give compound **9** as a yellow powder. Yield: 698 mg (1.11 mmol, 81 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.39$ (t, 1H; NH), 7.92–7.36 (m, 16H; Ar-H), 6.87 (t, 1H; NH), 5.42 (s, 2H; OCH_2), 5.37 (s, 2H; OCH_2), 3.77–3.70 (m, 6H; C*H*(CH_3)$_2$ and C*H*$_2$C*H*$_2$), 1.63 (d, 6H; CH(CH_3)$_2$), 1.40 ppm (d, 6H; CH(CH_3)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.0$, 166.1 (CO), 151.6, 146.9, 145.6, 143.5, 139.4, 136.4, 132.7, 129.0, 128.7, 126.8, 128.5, 128.1, 127.7, 127.6, 127.5, 127.2, 124.6, 124.3, 123.2, 117.3 (Ar-C), 76.4 (OCH_2), 71.3 (OCH_2), 40.4 (*C*H(CH_3)$_2$), 38.9, 37.2 (*C*H$_2$CH$_2$), 35.9 (*C*H(CH_3)$_2$), 22.9 (CH(*C*H$_3$)$_2$), 22.6 ppm (CH(*C*H$_3$)$_2$); elemental analysis calcd (%) for $C_{36}H_{40}N_2O_4S_2$: C 68.76, H 6.41, N 4.45; found: C 68.14, H 6.04, N 4.76.

1-[2,3-Di(benzyloxy)benzamido]-2-[2,3-di(isopropylmercapto)benzamido]-2,2′-dimethylethane (13): Compound **13** was prepared as described for **9** from 2,3-di(benzyloxy)benzoic acid chloride (457 mg, 1.37 mmol), NEt_3 (207 μL, 1.51 mmol) and compound **12** (467 mg, 1.37 mmol) in THF (30 mL). Yield: 827 mg (1.26 mmol, 92 %) of a yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.29$ (br.t, 1H; NH), 7.73 (dd, 1H; Ar-H), 7.62–7.25 (m, 15H; Ar-H), 6.67 (br.s, 1H; NH), 5.30 (s, 2H; OCH_2), 5.26 (s, 2H; OCH_2), 3.73 (d, 2H; C*H*$_2$C(CH$_3$)$_2$), 3.66–3.51 (m, 2H; C*H*(CH_3)$_2$), 1.50 (d, 6H; CH(CH_3)$_2$), 1.40 (s, 6H; C(CH_3)$_2$), 1.26 ppm (d, 6H; CH(*C*H$_3$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.9$, 167.0 (CO), 152.1, 147.1, 145.1, 145.0, 136.7, 129.5, 129.2, 129.1, 129.0, 128.9, 128.7, 128.6, 128.3, 128.2, 128.0, 127.9, 124.9, 124.7, 123.7, 117.7 (Ar-C), 76.7 (OCH_2), 71.9 (OCH_2), 56.0 (*C*H$_2$C(CH$_3$)$_2$), 48.6 (CH$_2$*C*(CH$_3$)$_2$), 40.8 (*C*H(CH$_3$)$_2$), 36.5 (*C*H(CH$_3$)$_2$), 24.9 (CH$_2$C(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$), 23.1 ppm (CH(*C*H$_3$)$_2$); elemental analysis calcd (%) for $C_{38}H_{44}N_2O_4S_2$: C 69.48, H 6.75, N 4.26; found: C 69.27, H 6.69, N 4.04.

1-[2,3-Di(benzyloxy)benzamido]-2-[2,3-di(isopropylmercapto)benzamido]benzene (17): A sample of 2,3-di(benzyloxy)benzoic acid chloride (726 mg, 1.98 mmol) was dissolved in THF (20 mL) and added dropwise to a solution of NEt_3 (0.720 μL, 4.95 mmol) and compound **16** (786 mg, 1.98 mmol) in THF (30 mL). The solution was stirred for 12 h and the NEt_3·HCl formed was then filtered off. The solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 (30 mL) and the organic layer was washed with aqueous solutions of NaOH (20 mL, 10 %), hydrochloric acid (20 mL, 2 M) and NaCl (20 mL, 35 %). The organic phase was dried with $MgSO_4$, the solvent was removed in vacuo and the crude product was purified by column chromatography (SiO_2, ethyl acetate) to give **17** as a yellow powder. Yield: 1.31 g (1.94 mmol, 98 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.89$ (s, 1H; NH), 8.31 (s, 1H; NH), 7.74–7.01 (m, 20H; Ar-H), 5.10 (s, 2H; OCH_2), 5.08 (s, 2H; OCH_2), 3.46–3.27 (m, 2H; C*H*(CH_3)$_2$), 1.29 (d, 6H; CH(C*H*$_3$)$_2$), 1.04 ppm (d, 6H; CH(C*H*$_3$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 180.1$, 167.9 (CO), 164.5, 152.2, 150.5, 149.3, 147.3, 146.0, 142.6, 136.8, 133.3, 131.3, 130.9, 130.7, 129.5, 129.2, 129.1, 128.7, 128.1, 127.6, 126.6, 126.3, 125.4, 125.2, 124.9, 124.3, 124.1, 118.4 (Ar-C), 77.3 (OCH_2), 71.9 (OCH_2), 40.8 (*C*H(CH$_3$)$_2$), 36.6 (*C*H(CH$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$), 23.1 ppm (CH(*C*H$_3$)$_2$); elemental analysis calcd (%) for $C_{40}H_{40}N_2O_4S_2$: C 70.98, H 5.96, N 4.14; found: C 70.57, H 5.88, N 3.76.

1-[2,3-Di(benzyloxy)benzamido]-4-[2,3-di(isopropylmercapto)benzamido]benzene (21): Compound **21** was prepared as described for **17** from 2,3-di(benzyloxy)benzoic acid chloride (726 mg, 1.98 mmol), NEt_3 (0.72 mL, 4.95 mmol) and compound **20** (786 mg, 1.98 mmol). Yield: 1.27 g (1.88 mmol, 95 %) of a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.28$ (s, 1H; NH), 9.18 (s, 1H; NH), 8.07 (dd, 1H; Ar-H), 7.85–7.34 (m, 19H; Ar-H), 5.43 (s, 2H; OCH_2), 5.40 (s, 2H; OCH_2), 3.73 (sept, 1H; C*H*(CH_3)$_2$), 3.65 (sept, 1H; C*H*(CH_3)$_2$), 1.63 (d, 6H; CH(C*H*$_3$)$_2$), 1.46 ppm (d, 6H; C*H*(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 166.1, 162.9 (CO), 151.7, 145.7, 138.7, 138.3, 136.2, 135.7, 129.4, 129.3, 129.0, 128.8, 128.7, 128.6, 128.3, 128.2, 127.6, 126.7, 125.8, 124.6, 123.5, 117.5, 115.8, 115.6, 114.3, 111.2 (Ar-C), 76.7 (OCH_2), 71.4 (OCH_2), 41.1 (*C*H(CH_3)$_2$), 36.2 (*C*H(CH$_3$)$_2$), 23.0 (CH(*C*H$_3$)$_2$), 22.6 ppm (CH(*C*H$_3$)$_2$); elemental analysis calcd (%) for $C_{40}H_{40}N_2O_4S_2$: C 70.98, H 5.96, N 4.14; found: C 70.36, H 5.89, N 3.82.

General procedure for the preparation of the ligands H_4-1–H_4-4: The ligand precursors **9**, **13**, **17** and **21** and naphthalene (1.25 equiv per protecting group) were dissolved in THF. Pieces of sodium (2.5 equiv per protecting group) were added and the solutions were stirred for 12 h at ambient temperature. Methanol (5 mL) was added and the stirring was continued for 15 min. The solvents were then removed in vacuo and the residue was dissolved in degassed water (50 mL). The aqueous phase was washed with diethyl ether (3 × 20 mL) and filtered. Hydrochloric acid was added and the precipitate obtained was isolated by filtration, washed with water and diethyl ether, and dried in vacuo.

1-(2,3-Dihydroxybenzamido)-2-(2,3-dimercaptobenzamido)-2,2′-dimethylethane (H_4-1): Prepared from 2 mmol of compound **13**. Yield: 96 %. ^{1}H NMR (300 MHz, [D_7]DMF): $\delta = 10.44$ (br.s, 2H; OH), 9.10 (t, 1H; NH), 8.25 (s, 1H; NH), 7.60 (d, $J = 7.8$ Hz, 1H; Ar-H), 7.49 (d, $J =$ 8.2 Hz, 1H; Ar-H), 7.35 (d, $J = 7.8$ Hz, 1H; Ar-H), 7.12 (t, $J = 7.8$ Hz, 1H; Ar-H), 7.05 (d, $J = 8.2$ Hz, 1H; Ar-H), 6.78 (t, $J = 8.2$ Hz, 1H; Ar-H), 5.59 (br.s, 2H; SH), 3.82 (d, 2H; C(Me$_2$)-C*H*$_2$), 1.56 ppm (s, 6H; C-(CH$_3$)$_2$); ^{13}C NMR (75 MHz, [D_7]DMF): $\delta = 171.4$, 169.9 (CO), 150.6, 147.5, 137.6, 134.0, 131.6, 130.6, 126.1, 125.6, 119.5, 118.8, 118.0, 116.1 (Ar-C), 56.1 (*C*H$_2$C(CH$_3$)$_2$), 48.4 (CH$_2$*C*(CH$_3$)$_2$), 24.9 ppm (CH$_2$C(*C*H$_3$)$_2$); IR (KBr): $\tilde{\nu} = 3307$ (s, OH), 3064 (m, Ar-H), 2973 (m, CH), 2534 (w, SH), 1641 (s, C=O), 1588, 1523 cm^{-1} (s, NH); elemental analysis calcd (%) for $C_{18}H_{20}N_2O_4S_2$: C 55.08, H 5.14, N 7.14; found: C 54.78, H 5.06, N 6.87.

1-(2,3-Dihydroxybenzamido)-2-(2,3-dimercaptobenzamido)ethane (H_4-2): Prepared from 2 mmol of compound **9**. Yield: 91 %. ^{1}H NMR (400 MHz, [D_7]DMF): $\delta = 13.00$ (br.s, 2H; OH), 9.10 (s, 1H; NH), 8.83 (s, 1H; NH), 7.59 (d, $J = 7.8$ Hz, 1H; Ar-H), 7.47 (d, $J = 7.8$ Hz, 1H; Ar-H), 7.45 (d, $J = 8.0$ Hz, 1H; Ar-H), 7.08 (t, $J = 7.8$ Hz, 1H; Ar-H), 7.00 (d, $J = 8.0$ Hz, 1H; Ar-H), 6.71 (t, $J = 8.0$ Hz, 1H; Ar-H), 5.93 (br.s, 2H; SH), 3.63 ppm (s, 4H; C*H*$_2$C*H*$_2$); ^{13}C NMR (100 MHz, [D_7]DMF): $\delta = 170.7$, 169.3 (CO), 150.2, 146.7, 134.5, 133.2, 131.6, 131.3, 125.6, 124.6, 118.7, 117.9, 117.2, 115.0 (Ar-C), 39.1 ppm (*C*H$_2$C*H*$_2$); IR (KBr): $\tilde{\nu} = 3363$ (s, OH), 3057 (m, Ar-H), 2935 (w, C-H), 2528 (m, SH), 1639 (s, C=O), 1588 (s, NH), 1458, 1328, 1263, 1173, 742 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{16}N_2O_4S_2$: C 52.73, H 4.43, N 7.69; found: C 51.70, H 4.49, N 6.48.

1-(2,3-Dihydroxybenzamido)-2-(2,3-dimercaptobenzamido)benzene (H_4-3): Prepared from 2 mmol of compound **17**. Yield: 90 %. ^{1}H NMR (300 MHz, [D_7]DMF): $\delta = 11.34$ (s, 2H; OH), 10.50 (s, 1H; NH), 10.41 (s, 1H; NH), 8.10–6.81 (m, 10H; Ar-H), 5.86 ppm (s, 2H; SH); ^{13}C NMR (75 MHz, [D_7]DMF): $\delta = 168.9$, 168.8 (CO), 150.0, 147.5, 136.5, 134.8, 132.3, 132.2, 131.9, 130.4, 128.5, 126.9, 126.5, 126.4, 126.3, 125.9, 119.9,

119.2, 119.0, 117.2 ppm (Ar-C); IR (KBr): $\tilde{\nu}=3270$ (s, OH), 3063 (m, Ar-H), 2532 (w, SH), 1645 (s, C=O), 1596, 1523 cm^{-1} (s, NH); elemental analysis calcd (%) for $C_{20}H_{16}N_2O_4S_2$: C 58.24, H 3.91, N 6.79; found: C 57.64, H 4.40, N 6.50.

1-(2,3-Dihydroxybenzamido)-4-(2,3-dimercaptobenzamido)benzene (H_4-4): Prepared from 2 mmol of compound **21**. Yield: 95%. ^{1}H NMR (300 MHz, [D$_7$]DMF): $\delta=11.94$ (br.s, 2H; OH), 10.53 (s, 1H; NH), 10.51 (s, 1H; NH), 7.96–7.86 (m, 4H; Ar-H), 7.71–7.67 (m, 2H; Ar-H), 7.53 (d, 1H; Ar-H), 7.21 (t, 1H; Ar-H), 7.13 (d, 1H; Ar-H), 6.83 (t, 1H; Ar-H), 6.07 ppm (br.s, 2H; SH); ^{13}C NMR (75 MHz, [D$_7$]DMF): $\delta=169.1$, 167.9 (CO), 150.2, 147.5, 137.3, 136.5, 135.1, 134.6, 132.0, 130.7, 126.2, 125.9, 122.4, 120.9, 119.9, 119.0, 118.8, 117.1 ppm (Ar-C); IR (KBr): $\tilde{\nu}=3290$ (s, OH), 3008 (m, Ar-H), 2551 (w, SH), 1644 (s, C=O) 1448, 1522 cm^{-1} (s, NH); elemental analysis calcd (%) for $C_{20}H_{16}N_2O_4S_2$: C 58.24, H 3.91, N 6.79; found: C 58.21, H 4.03, N 6.53.

$(AsPh_4)_2[Ti_2(2)_2(\mu\text{-}OCH_3)_2]$ $(AsPh_4)_2$[22]: Ligand H_4-**2** (106 mg, 0.29 mmol), [TiO(acac)$_2$] (51 mg, 0.19 mmol) and Na_2CO_3 (21 mg, 0.19 mmol) were dissolved in methanol (20 mL) and the solution was stirred for 12 h at ambient temperature. Ph_4AsCl (81 mg, 0.19 mmol) was then added to the reaction mixture and the red solution was filtered. Diffusion of diethyl ether into the filtrate at room temperature gave $(AsPh_4)_2$[**22**] as a dark red powder. Yield: 25 mg (0.015 mmol). ^{1}H NMR (600 MHz, [D$_7$]DMF): $\delta=10.26$ (s; NH), 10.08 (s; NH), 9.19 (s; NH), 8.49 (s; NH), 7.98–7.84 (m, 40H; $AsPh_4$-H), 7.11, 7.06, 6.93, 6.92, 6.91, 6.81, 6.80, 6.73 (d; Ar-H), 6.72 (t; Ar-H), 6.70 (d; Ar-H), 6.50, 6.49, 6.42 (t; Ar-H), 6.25 (d; Ar-H), 6.21, 6.19 (t; Ar-H), 6.10, 6.05 (d; Ar-H), 4.52 (s, 3H; OCH_3), 4.38 (s, 3H; OCH_3), 3.90–3.17 ppm (m, 8H; CH_2CH_2); ^{13}C NMR (150 MHz, [D$_7$]DMF): $\delta=170.7$, 170.2, 168.2, 168.1, 167.8, 166.9 (CO), 162.2, 161.8, 160.2, 160.0, 157.4, 155.7, 147.9, 147.6, 136.5 (9× Ar-C), 135.1 ($AsPh_4$-C), 134.9 (Ar-C), 134.2, 131.7 (2×$AsPh_4$-C), 128.5, 127.5, 127.1, 126.7, 122.4, 122.1, 121.4, 121.3, 121.1, 120.6, 120.3, 120.1, 119.8, 119.7, 119.2, 119.1, 117.9, 117.7, 117.0, 116.4, 115.8, 115.7, 115.4, 115.3, 111.9, 111.6 (26×Ar-C), 64.4, 61.3 (CH_3), 39.9, 39.8, 39.5, 38.9, 38.6, 38.3 ppm (CH_2); only three of the expected four $AsPh_4$ carbon resonances were detected in the ^{13}C NMR spectrum; MS (MALDI, negative ions): m/z 1260 $[(AsPh_4)Ti_2(\mathbf{1})_2(OCH_3)_2]^-$; IR (KBr): $\tilde{\nu}=3413$ (m, NH), 3055 (w, Ar-H), 2922, 2817 (w, C-H), 1641 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{82}H_{70}As_2N_4O_{10}S_4Ti_2$: C 59.86, H 4.29, N 3.41; found: C 59.16, H 4.42, N 3.89.

$(PNP)_2[Ti_2(3)_2(\mu\text{-}OCH_3)_2]$ $(PNP)_2$[23]: Ligand H_4-**3** (74 mg, 0.25 mmol), [TiO(acac)$_2$] (45 mg, 0.17 mmol) and Na_2CO_3 (18 mg, 0.17 mmol) were dissolved in methanol and the solution was stirred for 12 h at ambient temperature. (PNP)Cl (69 mg, 0.17 mmol) was then added and the red precipitate that formed was isolated by filtration, washed with methanol and dried in vacuo. The crude product was purified by recrystallisation from acetone/diethyl ether to give 61 mg (0.03 mmol) of $(PNP)_2$[**23**] as red crystals. ^{1}H NMR (600 MHz, [D$_7$]DMF): $\delta=10.19$ (s, 1H; NH), 9.30 (s, 1H; NH), 8.73 (d, 1H; Ar-H), 8.00–7.87 (m, 60H; PNP-H), 7.50 (d, 1H; Ar-H), 7.35 (dt, 1H; Ar-H), 7.26 (d, 1H; Ar-H), 7.16 (dt, 1H; Ar-H), 7.13 (d, 1H; Ar-H), 6.91 (d, 1H; Ar-H), 6.87 (t, 1H; Ar-H), 6.54 (t, 1H; Ar-H), 6.44 (d, 1H; Ar-H), 4.48 ppm (s, 6H; OCH_3); ^{13}C NMR (150 MHz, [D$_7$]DMF): $\delta=167.9$, 166.7 (CO), 160.9, 160.6, 156.1, 144.8, 136.4, 135.3, 135.1, 134.2, 131.7, 131.3, 128.7, 127.8, 127.3, 124.5, 124.3, 123.3, 122.1, 120.7, 119.7, 117.9, 116.7, 113.7 (PNP-C and Ar-C), 65.6 ppm (OCH_3); MS (ESI, negative ions): m/z 487.1 $[Ti_2(\mathbf{3})_2(OCH_3)_2]^{2-}$; elemental analysis calcd (%) for $C_{114}H_{90}N_6O_{10}P_4S_4Ti_2$: C 66.73, H 4.42, N 4.10; found: C 67.30, H 4.10, N 3.88.

$(PNP)_4[Ti_2(3)_3]$ $(PNP)_4$[24]: Ligand H_4-**3** (104 mg, 0.25 mmol), [TiO(acac)$_2$] (45 mg, 0.17 mmol) and Na_2CO_3 (18 mg, 0.17 mol) were dissolved in methanol (20 mL) and the solution was stirred for 12 h at 50 °C. (PNP)Cl (69 mg, 0.17 mmol) was then added and the solvent was removed in vacuo. Recrystallisation from methanol/diethyl ether gave 76 mg (0.022 mmol) of $(PNP)_4$[**24**] as a red solid. ^{1}H NMR (600 MHz, [D$_7$]DMF): $\delta=12.03$ (s; NH), 11.87 (s; NH), 11.04 (br.s; NH), 10.99 (s; NH), 10.70 (s; NH), 7.96–7.82 (m; Ar-H), 7.75–7.56 (m; Ar-H), 7.34–7.20 (m; Ar-H), 7.05 (dd; Ar-H), 7.01 (dd; Ar-H), 6.93 (dd; Ar-H), 6.73 (t; Ar-H), 6.69 (t; Ar-H), 6.63 (t; Ar-H), 6.57–6.54 (m; Ar-H), 6.53 (t; Ar-H), 6.46 (t; Ar-H), 6.39 (t; Ar-H), 6.28 ppm (dd; Ar-H); the two geometrical isomers of [**24**]$^{4-}$ (parallel and antiparallel) lead to overlapping signals, which could not be resolved in the ^{1}H NMR spectrum; ^{13}C NMR (150 MHz, [D$_7$]DMF): $\delta=171.4$, 171.2, 171.1, 169.5, 169.4, 169.2 (CO), 165.5, 165.4, 165.3, 165.1, 158.5, 158.4, 158.3, 156.0, 140.4, 140.1, 139.4, 138.2, 137.8, 136.9, 134.1, 133.1, 132.3, 131.5, 128.4, 126.4, 124.4, 124.3, 124.2, 123.9, 123.8, 123.7, 122.1, 120.6, 120.3, 120.2, 117.2, 117.1 ppm (Ar-C). The two geometrical isomers of [**24**]$^{4-}$ (parallel and antiparallel) should give rise to a total of 54 resonances in the ^{13}C NMR spectrum; these could not all be resolved; MS (ESI, negative ions): m/z 1198.7 $[(PNP)_2[Ti_2(\mathbf{3})_3]]^{2-}$, 619.5 $[(PNP)[Ti_2(\mathbf{3})_3]]^{3-}$, 440.3 $[H[Ti_2(\mathbf{3})_3]]^{3-}$; elemental analysis calcd (%) for $C_{204}H_{156}N_{10}O_{12}P_8S_6Ti_2$: C 70.50, H 4.52, N 4.03; found: C 70.31, H 4.42, N 3.89.

$Na(PNP)_3[Ti_2(1)_3]$ $Na(PNP)_3$[25]: Ligand H_4-**1** (104 mg, 0.26 mmol), [TiO(acac)$_2$] (45 mg, 0.17 mmol) and Na_2CO_3 (18 mg, 0.17 mmol) were dissolved in degassed methanol (20 mL). The solution was stirred for 12 h at ambient temperature and (PNP)Cl (98 mg, 0.17 mmol) was then added. The solution was filtered and the solvent was removed in vacuo. The crude product was recrystallised from methanol/diethyl ether to give 60 mg (0.02 mmol, 23%) of $Na(PNP)_3[Ti_2(\mathbf{1})_3]\cdot CH_3OH\cdot H_2O\cdot Et_2O$. ^{1}H NMR (500 MHz, [D$_7$]DMF, solvent-free compound): $\delta=9.80$ (br.t, 3H; NH), 8.14 (br.s, 3H; NH), 7.80–7.60 (m, 90H; PNP Ar-H), 7.15 (d, $^3J=7.8$ Hz, 3H; Ar-H), 7.08 (d, $^3J=7.5$ Hz, 3H; Ar-H), 6.98 (d, $^3J=7.5$ Hz, 3H; Ar-H), 6.65 (t, $^3J=7.5$ Hz, 3H; Ar-H), 6.32 (t, $^3J=7.8$ Hz, 3H; Ar-H), 6.21 (d, $^3J=7.8$ Hz, 3H; Ar-H), 4.81 (br.s, 6H; CH_2), 1.38 ppm (br.s, 18H; CH_3); ^{13}C NMR (125 MHz, [D$_7$]DMF, solvent-free compound): $\delta=169.41$, 167.44 (CO), 161.81, 161.40, 155.24, 152.05, 135.63 (5×Ar-C), 134.34, 133.08, 133.03, 132.98, 130.24, 130.19, 130.11, 128.48, 128.46, 127.62 (Ar-C and PNP-C), 128.22, 123.03, 121.85, 117.86, 116.47, 115.56, 112.29 (Ar-C), 54.980 ($CH_2C(CH_3)_2$), 49.46 ($CH_2C(CH_3)_2$), 25.16 ppm (br; $CH_2C(CH_3)_2$); MS (ESI, negative ions): m/z 630.7 $[Ti_2(\mathbf{1})_3+2H]^{2-}$; elemental analysis calcd (%) for solvent-free $Na(PNP)_3$[**25**] $C_{162}H_{138}N_9NaO_{12}P_6S_6Ti_2$: C 67.10, H 4.80, N 4.35; found: C 66.67, H 4.95, N 4.10.

$Na(PNP)_3[Ti_2(4)_3]$ $Na(PNP)_3$[26]: Ligand H_4-**4** (103 mg, 0.25 mmol), [TiO(acac)$_2$] (45 mg, 0.17 mmol) and Na_2CO_3 (18 mg, 0.17 mol) were dissolved in degassed methanol (20 mL) and the solution was stirred for 16 h at ambient temperature. (PNP)Cl (98 mg, 0.17 mmol) was then added and the solution was filtered. Removal of the solvent gave a red solid. Recrystallisation from methanol/diethyl ether gave 95 mg (0.032 mmol, 38%) of $Na(PNP)_3$[**26**] as a red solid. ^{1}H NMR (500 MHz, [D$_7$]DMF): $\delta=12.01$ (t, 3H; NH), 10.68 (s, 3H; NH), 7.90–7.60 (m, 90H; PNP Ar-H), 7.32 (d, $^3J=8.6$ Hz, 3H; Ar-H), 7.22 (d, $^3J=7.5$ Hz, 3H; Ar-H), 7.06 (d, $^3J=8.6$ Hz, 3H; Ar-H), 6.74 (t, $^3J=8.6$ Hz, 3H; Ar-H), 6.41 (t, $^3J=7.5$ Hz, 3H; Ar-H), 6.30 (d, $^3J=7.5$ Hz, 3H; Ar-H), 7.95 ppm (m, 12H; Ar-H); ^{13}C NMR (125 MHz, [D$_7$]DMF): $\delta=167.9$, 166.3 (CO), 162.2, 161.9, 155.1, 152.7, 136.8, 136.2 (Ar-C), 135.0 (PNP Ar-C), 134.6 (Ar-C), 133.7 (PNP Ar-C), 133.6 (PNP Ar-C), 130.9 (PNP Ar-C), 130.8 (PNP Ar-C), 130.7 (PNP Ar-C), 129.8, 129.1, 128.2, 125.1, 123.1, 121.1, 120.7, 118.8, 116.9 ppm (Ar-C); six instead of the expected four resonances for the PNP cations were observed; MS (MALDI, negative ions): m/z 2936 $[(PNP)_3[Ti_2(\mathbf{4})_3]]^-$, 2398 $[H(PNP)_2[Ti_2(\mathbf{8})_3]]^-$; elemental analysis calcd (%) for $C_{168}H_{126}N_9NaO_{12}P_6S_6Ti_2$: C 68.17, H 4.29, N 4.26; found: C 69.10, H 4.41, N 4.14.

X-ray crystallography: $(AsPh_4)_2$[**22**] was crystallised as its methanol solvate $(AsPh_4)_2$[**22**]·2 CH_3OH by slow diffusion of diethyl ether into a methanolic solution of $(AsPh_4)_2$[**22**] at room temperature. Crystals of compound $(PNP)_2$[**23**] were obtained by recrystallisation from acetone/diethyl ether. The solvate $Na(PNP)_3$[**25**]·$CH_3OH\cdot H_2O\cdot Et_2O$ was obtained by diffusion of diethyl ether into a methanolic solution of $Na(PNP)_3$[**25**] at room temperature. Crystals of $Na_{1.5}(PNP)_{6.5}$[**26**]$_2$·3 DMF were obtained by diffusion of diethyl ether into a DMF solution of $Na(PNP)_3$[**26**] at room temperature.

X-ray diffraction data were collected at −75 °C ($(AsPh_4)_2$[**22**] and $Na_{1.5}(PNP)_{6.5}$[**26**]$_2$·3 DMF) on an Enraf–Nonius Kappa CCD diffractometer or at −120 °C ($(PNP)_2$[**23**] and $Na(PNP)_3$[**25**]·$CH_3OH\cdot H_2O\cdot Et_2O$) on a Bruker AXS APEX diffractometer, both equipped with a rotating anode and with $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). Empirical absorption corrections using the program SORTAV[28] were applied to the raw data for

$(AsPh_4)_2$[**22**]·2 CH_3OH ($0.84 \le T \le 0.92$) and $Na_{1.5}(PNP)_{6.5}$[**26**]$_2$·3 DMF ($0.88 \le T \le 0.96$). The program SADABS[29] was used for absorption corrections to the raw data of $(PNP)_2$[**23**] ($0.94 \le T \le 0.99$) and $Na(PNP)_3$[**25**]·CH_3OH·H_2O·Et_2O ($0.97 \le T \le 0.99$). Structure solutions were performed with SHELXS[30] in all cases and the refinement was carried out with SHELXL[31] using anisotropic thermal parameters for all non-hydrogen atoms (for exceptions see below). Hydrogen atoms were added to the structure models at calculated positions and refined as riding atoms. Owing to the cell dimensions, data collection was done with a crystal to detector distance of 130 mm for $Na_{1.5}(PNP)_{6.5}$[**26**]$_2$·3 DMF. As a result, the number of observed reflections is limited. The positional parameters of the carbon atoms of the cations and the solvent molecule in the asymmetric unit were refined with isotropic thermal parameters. One nitrogen atom of one PNP cation was refined with split positions. Due to the limited number of observed intensities we could not clearly localize one half PNP cation. Alternatively, there could be one disordered half sodium cation in the asymmetric unit. The exact composition of the crystalline compound $Na_2(PNP)_6$[**26**]$_2$·3 DMF or $Na(PNP)_7$[**26**]$_2$·3 DMF could therefore not be determined unambiguously and the average value $Na_{1.5}(PNP)_{6.5}$[**26**]$_2$·3 DMF was taken as the correct composition of the crystalline material. Additional crystal, data collection and refinement details are summarised in Table 3.

CCDC-226389 ($(AsPh_4)_2$[**22**]·2 CH_3OH), CCDC-616878 ($(PNP)_2$[**23**]), CCDC-234748 ($Na(PNP)_3$[**25**]·CH_3OH·H_2O·Et_2O) and CCDC-617314 ($Na_{1.5}(PNP)_{6.5}$[**26**]$_2$·3 DMF) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 3. Crystallographic data for $(AsPh_4)_2$[**22**]·2 CH_3OH, $(PNP)_2$[**23**], $Na(PNP)_3$[**25**]·CH_3OH·H_2O·Et_2O and $Na_{1.5}(PNP)_{6.5}$[**26**]$_2$·3 DMF.

	$(AsPh_4)_2$[**22**]·2 CH_3OH	$(PNP)_2$[**23**]	$Na(PNP)_3$[**25**]·CH_3OH·H_2O·Et_2O	$Na_{1.5}(PNP)_{6.5}$[**26**]$_2$·3 DMF
chem. formula	$C_{84}H_{78}As_2N_4O_{12}S_4Ti_2$	$C_{114}H_{90}N_6O_{10}P_4S_4Ti_2$	$C_{167}H_{154}N_9NaO_{15}P_6S_6Ti_2$	$C_{363}H_{288}N_{21.5}Na_{1.5}O_{27}P_{13}S_{12}Ti_4$
cryst. size [mm]	0.15×0.15×0.05	0.15×0.06×0.02	0.10×0.07×0.04	0.50×0.45×0.15
colour	red	red	red	red
Fw	1709.38	2051.84	3023.96	6396.56
space group	$P\bar{1}$ (no. 2)	$P1$ (no. 1)	$P1$ (no. 1)	$R\bar{3}c$ (no. 167)
a [Å]	11.493(1)	13.186(2)	13.594(3)	24.236(1)
b [Å]	12.771(1)	14.528(2)	17.190(4)	24.236(1)
c [Å]	15.029(1)	14.556(2)	18.900(4)	225.276(6)
α [°]	67.69(1)	73.040(3)	66.722(4)	90
β [°]	83.54(1)	73.040(3)	79.188(4)	90
γ [°]	75.44(1)	68.401(3)	82.523(4)	120
V [Å^3]	1974.9(3)	24.33.8(5)	3977.6(15)	114595(7)
Z	1	1	1	12
λ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	198(2)	123(2)	123(2)	198(2)
ρ calcd [g cm^{-3}]	1.437	1.400	1.262	1.112
refl. collected/$2\Theta_{max}$	10456/50.0	19327/50.0	24856/45.2	115369/45.0
unique reflns	6936	16293	20191	16319
refl. obs. ($I > 2\sigma(I)$)	5068	10465	13406	6684
no. of parameters/restr	574/0	1280/16293	1932/3	744/0
μ [mm^{-1}]	1.204	0.382	0.306	0.262
$R1$ ($I > 2\sigma(I)$)	0.068	0.070	0.077	0.187
$wR2$ (all data)	0.153	0.144	0.188	0.464
GOF	1.058	0.990	0.994	2.258
residual density [e Å^{-3}]	+0.709/−0.909	+0.690/−0.389	+1.297/−0.342	+1.474/−0.739

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