Synthesis and Coordination Chemistry of a Tris(benzene-*o*-dithiolato)-functionalized Ligand as a Siderophore Analog

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

As a siderophore analog, the tripodal tris(benzene-*o*-dithiol)-functionalized ligand H_6-**5**, has been synthesized in four steps including the reaction of 1,3,5-(triaminomethyl)-2,4,6-triethylbenzene and 2,3-bis(isopropylmercapto)benzoyl chloride followed by removal of the S-protecting groups. Reaction of compound H_6-**5** with $[Ti(OPr)_4]$ in the presence of $(NEt_4)Cl$ leads to the formation of complex $(NEt_4)_2[Ti(\mathbf{5})]$ featuring three bidentate benzene-*o*-dithiolato donors from one ligand coordinated to the metal center. An X-ray diffraction structure analysis with crystals of $(NEt_4)_2[Ti(\mathbf{5})]\cdot DMF$ has shown that the coordination geometry at the metal center is best described as distorted trigonal-prismatic with a twist angle of $\phi_{av} = 18.5°$.

Key words: Tripods, Benzene-*o*-dithiolato Ligand, X-Ray Diffraction, Titanium

Introduction

Siderophores are known as effective chelating ligands which mediate iron uptake in microorganisms. These low molecular weight compounds exhibit mostly oxygen donor groups [1, 2]. Enterobactin H_6-**A** (Fig. 1) is a tri(catechoylamide) and a typical example for a catechol-based siderophore. It is a powerful chelator and its iron(III) complex shows a high formal stability constant of $K_f = 10^{49}$ [3, 4]. Up to now the molecular structure of the $[Fe(\mathbf{A})]^{3-}$ complex has not been established by X-ray diffraction techniques, but the molecular structure of $K_2[V(\mathbf{A})]$ is known [5]. Synthetic analogs of enterobactin like TRENCAM H_6-**B** have been prepared to mimick the superb iron(III) uptake properties of enterobactin [6 – 11].

While a large number of oxygen-donor siderophores and their synthetic analogs are known, siderophore-analogous tripodal ligands with sulfur donor atoms have been less studied. A number of simple tripods with three monodentate nitrogen [12, 13] or sulfur donor atoms [14, 15] have been described. The introduction of a bidentate benzene-*o*-dithiolato donor group into a tripodal ligand, however, proved difficult. The bidentate benzene-*o*-dithiolato (bdt^{2-}) donor group is of special interest as it is known that selected transition metal complexes of type $[M(bdt)_3]^{n-}$ (M = Mo, W; $n = 0, 1, 2$) adopt a coordination geometry (octahedral or trigonal-prismatic) which depends on the formal oxidation state of the metal center [16 – 21].

We have become engaged in the coordination chemistry of tripodal tris(benzene-*o*-dithiolato) ligands, where the influence of the ligand backbone on the coordination chemistry and the redox properties of the metal complexes were of special interest. Up to now only very few tripodal ligands with benzene-*o*-dithiolato donor groups have been mentioned in the literature [22, 23]. In this contribution we describe the preparation of the novel tris(benzene-*o*-dithiol) ligand H_6-**5** (Scheme 1) and its coordination chemistry with titanium(IV).

Results and Discussion

The first step in the synthesis of tripod H_6-**5** was the conversion of 1,3,5-triethylbenzene into 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene **1**. The subsequent reaction of **1** with NaN_3 led to the formation

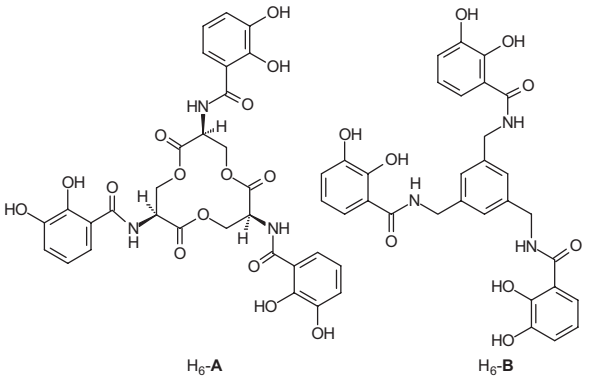
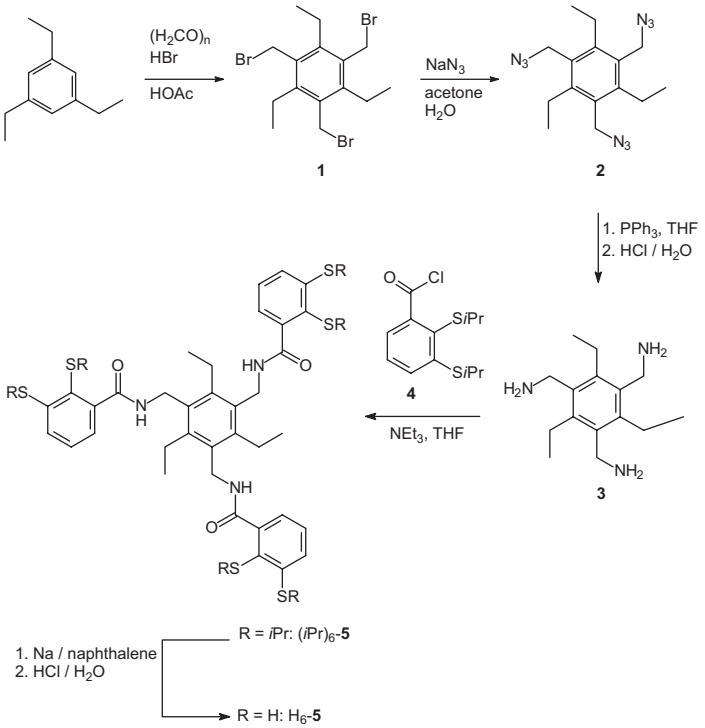


Fig. 1. Protonated enterobactin H_6-**A** and the synthetic analog TRENCAM H_6-**B**.

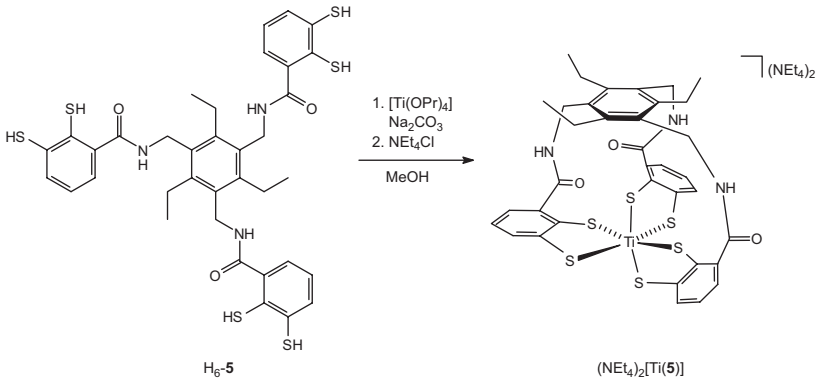
of the triazide **2** (Scheme 1). 1,3,5-Tris(aminomethyl)-2,4,6-triethylbenzene **3** was prepared from **2** using a protocol described previously [24]. The triamine **3** reacts with **4**, which was obtained by chlorination of 2,3-di(isopropylmercapto)benzoic acid [25, 26] with oxalyl chloride to give the ligand precursor (iPr)$_6$-**5**. Cleavage of the S-isopropyl bonds in (iPr)$_6$-**5** with sodium/naphthalene in THF yielded, after hydrolysis, the free ligand H_6-**5**.

Reaction of one equivalent of H_6-**5** with one equivalent of [Ti(OPr)$_4$] in the presence of Na_2CO_3 as a base in methanol resulted in a deep-red color of the solution ($\lambda_{max} = 534$ nm), which is typical of the $\{TiS_6\}^{2-}$ chromophore (Scheme 2) [27]. After addition of two equivalents of (NEt_4)Cl to the solution a dark-red precipitate formed. This precipitate was isolated and identified as the mononuclear complex (NEt_4)$_2$[Ti(**5**)] by ^{1}H NMR and mass spectrometry. In the ESI mass spectrum (negative ions) the characteristic signal for the complex anion $[Ti(\mathbf{5})]^{2-}$ featuring a matching isotope pattern was detected at $m/z = 397.51534$ (calcd. 397.51648 for $[Ti(\mathbf{5})]^{2-}$).

Single crystals of (NEt_4)$_2$[Ti(**5**)]·DMF were obtained by slow vapor diffusion of diethyl ether into a saturated solution of (NEt_4)$_2$[Ti(**5**)] in DMF. The X-ray diffraction analysis with single crystals of (NEt_4)$_2$[Ti(**5**)]·DMF revealed that the compound crystallizes in the centrosymmetric space group $P2_1/c$ with $Z = 4$. The molecular structure of the anion $[Ti(\mathbf{5})]^{2-}$ is depicted in Fig. 2. Due to the centrosymmetric space



Scheme 1. Synthesis of the tris(benzene-*o*-dithiol) H_6-**5**.



Scheme 2. Preparation of the titanium complex $(NEt_4)_2$[Ti(**5**)].

group, the unit cell contains both the Λ and the Δ isomers. Figure 2 depicts the Λ isomer. The structure analysis revealed a distorted trigonal-prismatic coordination environment for the titanium atom with a calculated twist angle of $\phi_{av} = 18.5°$. In contrast to this, the analogous titanium(IV) complex with three unsubstituted benzene-*o*-dithiolato ligands shows a distorted octahedral coordination environment at the metal center [27]. The coordination geometry in anion $[Ti(\mathbf{5})]^{2-}$ in the solid state might be explained with interactions of one NEt_4^+ cation with the aromatic rings of two bdt^{2-} subunits (Fig. 2, right) which could have caused the observed reduction of the calculated twist angle.

The molecular structure determination has revealed that the NH groups of the ligand backbone are not directed towards the sulfur atoms in *ortho*-positions of the aromatic rings. Thus intramolecular N–H···S hydrogen bonds, in analogy to N-H···O contacts which are typical for tri(catechoylamide) complexes [7, 8], are not formed. This is also corroborated by ^{1}H NMR spectroscopy, which features the resonance for the NH protons of H_6-**5** and $(NEt_4)_2$[Ti(**5**)] at very similar chemical shifts (see Experimental Section).

The metric parameters observed for $[Ti(\mathbf{5})]^{2-}$ fall in the range previously reported for $[NH_2(CH_3)_2]_2[Ti(bdt)_3]$ [27] and related complexes containing a $\{Ti(bdt)_3\}^{2-}$ moiety [23, 27 – 35]. The five-membered C_2S_2Ti chelate rings in the anion $[Ti(\mathbf{5})]^{2-}$ are folded along the S···S axis with dihedral angles between the TiS_2 and the C_6 planes in the range of 18.2(1)-25.6(1)°. These angles are similar to those observed for the analogous complex with a mesitylene backbone [23]. In contrast to this, much larger dihedral angles have been observed for the complex anion $[Ti(bdt)_3]^{2-}$ [27] and related titanium(IV) complexes bearing unbridged bdt^{2-} ligands [36 – 38]. The smaller dihedral angles in $[Ti(\mathbf{5})]^{2-}$ thus indicate strain in the tripodal ligand caused by the central spacer. In solution, the C_3-symmetry of the complex ion $[Ti(\mathbf{5})]^{2-}$ leads to a very simple ^{1}H NMR spectrum with only one set of signals.

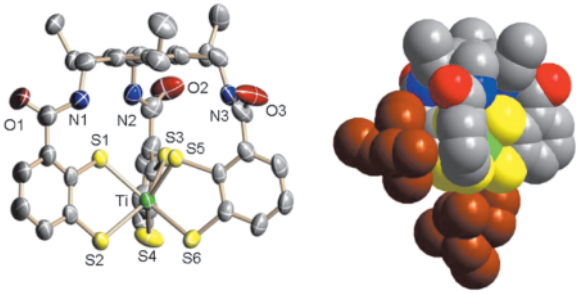


Fig. 2 (color online). Molecular structure of the complex dianion $[Ti(\mathbf{5})]^{2-}$ (left) in $(NEt_4)_2$[Ti(**5**)]·DMF. Hydrogen atoms have been omitted for clarity. In the space-filling model of $(NEt_4)_2$[Ti(**5**)] two counter ions are depicted in brown (right). Selected bond lengths (Å) and angles (deg): Ti–S1 2.404(2), Ti–S2 2.433(2), Ti–S3 2.402(2), Ti–S4 2.433(3), Ti–S5 2.421(2), Ti–S6 2.437(2); S1–Ti–S2 80.36(5), S1–Ti–S3 80.92(6), S1–Ti–S4 119.83(9), S1–Ti–S5 79.01(6), S1–Ti–S6 147.06(9), S2–Ti–S3 148.12(7), S2–Ti–S4 86.73(8), S2–Ti–S5 122.08(8), S2–Ti–S6 89.96(6), S3–Ti–S4 80.53(7), S3–Ti–S5 78.89(6), S3–Ti–S6 119.08(6), S4–Ti–S5 149.25(8), S4–Ti–S6 90.64(8), S5–Ti–S6 79.80(6).

Conclusion

We have described the second example for a tripodal tris(benzene-*o*-dithiol) ligand H_2-**5**, which is capable

of forming the titanium(IV) complex $(NEt_4)_2$[Ti(**5**)]. The $[Ti(\mathbf{5})]^{2-}$ complex dianion adopts the rare distorted trigonal-prismatic coordination geometry in the solid state which is possibly caused by interactions of the complex anion with the NEt_4^+ counter ions.

Experimental Section

Chemicals and solvents were purchased from Aldrich. NMR spectra were recorded on Bruker Avance II and Avance III spectrometers. Mass spectra were obtained with a Bruker Reflex IV, a Finnigan MAT95 or an Orbitrap XL spectrometer at the Institut für Anorganische und Analytische Chemie or the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster. UV/Vis spectra were measured with a Varian Cary 50 spectrometer. If not noted otherwise, all preparations were carried out in Schlenk flasks under an argon atmosphere. Compounds **3** [24] and **4** [25, 26] have been prepared according to published procedures.

*1,3,5-Tri(bromomethyl)-2,4,6-triethylbenzene (**1**)*

A mixture of 1,3,5-triethylbenzene (3.48 mL, 18.5 mmol), paraformaldehyde (7.03 g) and HBr in AcOH (33 wt.-%, 30 mL, 171 mmol) was heated to reflux for 6 days. The reaction mixture was quenched with ice water, and the formed precipitate was isolated by filtration and washed with water (3 × 50 mL). The solid residue was dissolved in CH_2Cl_2 (40 mL) and washed with brine (3 × 40 mL). The organic layer was separated, dried over $MgSO_4$, and filtered. The solvent was removed *in vacuo*. The pale-brown residue was sublimed at 145 °C *in vacuo* to give **1** as a colorless solid. Yield: 4.25 g (9.6 mmol, 52 %). – ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ = 4.58 (s, 6 , CH_2Br), 2.95 (q, ^3J = 7.6 Hz, 6 H, CH_2), 1.35 (t, ^3J = 7.6 Hz, 9 H, CH_3). – ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, ppm): δ = 145.0, 132.7 (Ar-C), 28.5 (CH_2Br), 22.7 (CH_2), 15.6 (CH_3). – MS (EI, 20 eV): m/z = 442 $[M+H]^+$, 361 $[M–Br]^+$. – $C_{15}H_{21}Br_3$ (441.04).

*1,3,5-Tris(azidomethyl)-2,4,6-triethylbenzene (**2**)*

CAUTION! NaN_3 has been found to be explosive under certain conditions and is highly toxic.

To a solution of **1** (2.68 g, 6.08 mmol) in acetone (25 mL) was added NaN_3 (1.58 g, 24.3 mmol). Water was added to the mixture which turned turbid. The suspension was heated to reflux for 12 h. The reaction mixture was then quenched with ice. The acetone was removed *in vacuo*, and the formed precipitate was isolated by filtration. Further purification was accomplished by recrystallization from hot ethanol. Yield: 1.04 g (3.18 mmol, 52 %). – ^{1}H NMR (200.1 MHz, $CDCl_3$, ppm): δ = 4.48 (s, 6 H, CH_2N_3), 2.84 (q, ^3J = 7.6 Hz, 6 H, CH_2), 1.22 (t, ^3J = 7.6 Hz, 9 H, CH_3). – ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, ppm): δ = 145.0, 130.0 (Ar-C), 48.0 (CH_2N_3), 23.6 (CH_2), 15.8 (CH_3). – MS (EI, 20 eV): m/z = 327 $[M]^+$, 285 $[M–N_3]^+$, 256 $[M–N_3–CH_2CH_3]^+$. – $C_{15}H_{21}N_9$ (327.39).

*1,3,5-Triethyl-2,4,6-tris[N-(2,3-di(isopropylmercapto)-benzamido)methyl]benzene (*i*Pr$_6$-**5**)*

Oxalyl chloride (2.58 mL, 29.5 mmol) was added dropwise to a mixture of 2,3-di(isopropylmercapto)benzoic acid (2.27 g, 8.91 mmol) and a few drops of DMF at 0 °C. After 20 min the ice bath was removed and the solution stirred at ambient temperature for 2 h. The oily 2,3-di(isopropylmercapto)benzoyl chloride obtained after removal of the solvent was redissolved in THF (15 mL). The resulting solution was added to a mixture of compound **3** (600 mg, 2.41 mmol) and NEt_3 (3.3 mL, 24 mmol) in THF (40 mL). The reaction mixture was stirred for 12 h at ambient temperature and after filtration to remove insolubles the solvent was removed *in vacuo*. The oily residue was purified by column chromatography (SiO_2, 1. CH_2Cl_2, 2. CH_2Cl_2-EtOAc = 1:1, v:v). After removal of the solvent compound *i*Pr$_6$-**5** was obtained as a beige solid. Yield: 2.06 g (2.05 mmol, 85 %). – ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm): δ = 7.35 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 3 H, Ar-H), 7.29 – 7.25 (m, 3 H, Ar-H), 7.22 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 3 H, Ar-H), 6.31 (t, ^3J = 4.4 Hz, 3 H, NH), 4.64 (d, ^3J = 4.4 Hz, 6 H, NCH_2), 3.48 – 3.39 (m, 6 H, C*H*(CH_3)$_2$), 2.84 (q, ^3J = 7.4 Hz, 6 H, CH_2), 1.32 (d, ^3J = 6.6 Hz, 18 H, CH(C*H*$_3$)$_2$), 1.26 (t, ^3J = 7.4 Hz, 9 H, CH_3), 1.13 (d, ^3J = 6.6 Hz, 18 H, CH(C*H*$_3$)$_2$). – ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 168.1 (C(O)NH), 145.7, 144.2, 142.9, 131.8, 129.0 (Ar-C$_{quart}$), 128.7, 127.7, 125.0 (Ar-C), 40.5 (*C*H(CH_3)$_2$), 38.6 (CH_2N), 35.9 (*C*H(CH_3)$_2$), 23.1 (CH_2), 22.9, 22.6 (CH(*C*H$_3$)$_2$), 16.4 (CH_3). – MS (MALDI, DHB, positive ions): m/z = 1028 $[M+Na]^+$. – $C_{54}H_{75}N_3O_3S_6$ (1005.41).

*1,3,5-Triethyl-2,4,6-tris[N-(2,3-dimercaptobenzamido)-methyl]benzene (H$_6$-**5**)*

Compound *i*Pr$_6$-**5** (1.50 g, 1.49 mmol) and naphthalene (1.53 g, 11.9 mmol) were dissolved in freshly distilled THF (40 mL), and freshly cut pieces of sodium (514 mg, 22.4 mmol) were added. The reaction mixture was stirred for 12 h at ambient temperature, and then methanol (10 mL) was added to consume the remaining sodium. The solvent was removed *in vacuo*. The solid residue obtained was redissolved in degassed water and washed with degassed diethyl ether (3 × 15 mL). Insoluble material was removed by filtration. The aqueous layer was separated and acidified with hydrochloric acid (37 %) to afford a colorless solid. The precip-

itate was isolated by filtration and washed twice with water and diethyl ether (10 mL each). Drying *in vacuo* yielded H_6-**5** as a colorless powder. Yield: 935 mg (1.24 mmol, 83 %). – ^{1}H NMR (400.1 MHz, [D$_7$]DMF, ppm): $\delta = 8.49$ (t, $^3J = 4.4$ Hz, 3 H, NH), 7.57 (dd, $^3J = 7.7$ Hz, $^4J = 1.4$ Hz, 3 H, Ar-H), 7.29 (dd, $^3J = 7.7$ Hz, $^4J = 1.4$ Hz, 3 H, Ar-H), 7.03 (t, $^3J = 7.7$ Hz, 3 H, Ar-H), 5.84 (s br, 6 H, SH), 4.68 (d, $^3J = 4.4$ Hz, 6 H, NCH_2), 2.96 (q, $^3J = 7.3$ Hz, 6 H, CH_2), 1.25 (t, $^3J = 7.3$ Hz, 9 H, CH_3). – ^{13}C{^{1}H} NMR (100.6 MHz, [D$_7$]DMF, ppm): $\delta = 169.3$ (C(O)NH), 144.7, 135.8, 134.1, 132.6, 131.8, 131.6, 126.3, 125.3 (Ar-C), 38.8 (CH_2N), 23.5 (CH_2), 16.6 (CH_3). – MS (MALDI, DHB, positive ions): $m/z = 776$ $[M + Na]^+$. – $C_{36}H_{39}N_3O_3S_6$ (753.13).

*(NEt$_4$)$_2$[Ti(**5**)]*

A sample of [Ti(OPr)$_4$] in CH_2Cl_2 (0.1 M solution, 1.11 mL, 0.111 mmol) was added to a solution of H_2-**5** (100 mg, 0.133 mmol) and Na_2CO_3 (117 mg, 1.11 mmol) in freshly distilled methanol (20 mL). The solution was stirred under argon at ambient temperature for 12 h and was then filtered. Addition of (NEt$_4$)Cl (77 mg, 0.46 mmol) to the filtrate yielded a deep-red precipitate, which was isolated by filtration, washed with methanol (2 × 10 mL) and dried *in vacuo*. Yield: 84 mg (0.08 mmol, 60 %). – ^{1}H NMR (400.1 MHz, [D$_7$]DMF, ppm): $\delta = 8.21$ (t, $^3J = 3.8$ Hz, 3 H, NH), 7.25 (d, $^3J = 7.4$ Hz, 3 H, Ar-H), 7.13 (d, $^3J = 7.6$ Hz, 3 H, Ar-H), 6.83 (d, $^3J = 7.6$ Hz, $^3J = 7.4$ Hz, 3 H, Ar-H), 4.59 (d, $^3J = 3.8$ Hz, 6 H, NCH_2), 3.28 – 3.16 (m br, 16 H, Et_3N-CH_2CH$_3$), 2.81 (q, $^3J = 7.2$ Hz, 6 H, CH_2), 1.27 (t, $^3J = 7.2$ Hz, 9 H, CH_3), 1.14 – 1.09 (m br, 24H, Et_3N-CH$_2$CH_3). – HRMS (ESI, negative ions): $m/z = 397.51534$ $[Ti(\mathbf{5})]^{2-}$ (calcd. 397.51648 for $[Ti(\mathbf{5})]^{2-}$). – UV/Vis (CH_3OH, nm): $\lambda_{max} = 534$. – $C_{52}H_{73}N_5O_3S_6Ti$ (1055.35). – Vapor diffusion of diethyl ether into a concentrated DMF solution of (NEt$_4$)$_2$[Ti(**5**)] yielded deep-red crystals of [Ti(**5**)](NEt$_4$)$_2$·DMF, which were suitable for an X-ray diffraction study.

*X-Ray structure determination of (NEt$_4$)$_2$[Ti(**5**)]·DMF*

Diffraction data of (NEt$_4$)$_2$[Ti(**5**)]·DMF were measured at 153(2) K using Cu K_α ($\lambda = 1.54178$ Å) radiation. Data were collected over the full sphere in the range $6.0° \le 2\theta \le 144.4°$. Structure solution and refinement [39] were achieved with standard Patterson and Fourier techniques, respectively. The asymmetric unit contains one dianion $[Ti(\mathbf{5})]^{2-}$, two NEt_4^+ cations and one DMF molecule. Two of the methyl groups of one of the NEt_4^+ cations are disordered, and the DMF molecule is also disordered over two positions (SOF 0.7 : 0.3). Non-hydrogen atoms were refined with anisotropic displacement parameters except for disordered atoms which were refined with isotropic displacement parameters. Hydrogen atoms bound to non-disordered atoms were added to the structure model on calculated positions (no hydrogen positions have been calculated for disordered atoms). *Selected crystallographic data*: Formula $C_{55}H_{80}N_6O_4S_6Ti$, $M_r = 1129.55$, red crystal, $0.48 \times 0.19 \times 0.03$ mm^3, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 12.667(3)$, $b = 17.509(3)$, $c = 26.830(5)$ Å, $\beta = 92.734(5)°$, $V = 5944(2)$ Å^3, $\rho_{calcd} = 1.26$ g cm^{-3}, $\mu = 3.6$ mm^{-1}, empirical absorption correction ($0.280 \le T \le 0.901$), 31547 intensities collected ($\pm h$, $\pm k$, $\pm l$), 9556 independent ($R_{int} = 0.0866$) and 6948 observed intensities [$I > 2\sigma(I)$], 665 refined parameters refined against all F^2, residuals for data with $I > 2\sigma(I)$: $R = 0.1074$, $wR = 0.2643$, for all data $R = 0.1406$, $wR = 0.2892$, largest peak / hole in last Difference Fourier map 1.12 / −0.65 e Å^{-3}. The refinement converged nicely but the disordered cation and solvent led to relatively high residuals.

CCDC 926583 contains 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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