Coordination chemistry of the sulfur analog of tricatechol siderophores

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Supplementary Information

Experimental Section

General Remarks

All operations were carried out under an atmosphere of dry argon using Schlenk and vacuum techniques. Solvents were dried by standard methods and freshly distilled prior to use. NMR spectra were recorded at 298 K with Bruker AC 200 (200 MHz) or Bruker AMX 400 (400 MHz) spectrometers and are reported relative to TMS as an internal standard or to the residual solvent signal. Mass spectra were obtained with Micromass Quattro LC-Z (ESI) or Bruker Reflex IV (MALDI) spectrometers. Elemental analyses were performed with a Vario EL III CHNS analyzer. Commercially available [Ti(OPr)4] (Aldrich) was used without further purification.

Ligands H6-1 and H2-2 were synthesized according to previously published methods.1

Selected analytical data for

H6-1: 1H NMR (400 MHz, DMF-d7, 25 °C, ppm): δ = 8.63 (t, 1H, N-H), 7.55 (dd, 3J = 7.5 Hz, 4J = 1.5 Hz, 3H, Ar-H), 7.30 (dd, 3J = 7.5 Hz, 4J = 1.5 Hz, 3H, Ar-H), 7.05 (t, 3J = 7.5 Hz, 3H, Ar-H), 4.66 (d, 3J = 3.8 Hz, 6H, CH2), 2.54 (s, 9H, CH3); 13C NMR (100 MHz, DMF-d7, 25 °C): δ = 169.4 (C(O)NH), 137.8, 134.0, 133.4, 132.8, 131.7, 126.3, 125.4, 125.0 (Ar-C), 39.7 (CH2), 16.5 (CH3); MS (MALDI) m/z = 711 [M–H]. Calcd for C33H33N3O3S6: C, 55.67; H, 4.67; N, 5.90; S, 27.02%. Found: C, 55.36; H, 4.43; N, 6.04; S, 25.88.

H2-2: 1H NMR (400 MHz, DMF-d7, 25 °C, ppm): δ = 9.07 (s br, 1H, N-H), 7.44 (d, 3J = 7.5 Hz, 2H, Ph-H), 7.43 (d, 3J = 7.5 Hz, 1H, Ph-H), 7.36 (t, 3J = 7.5 Hz, 2H, Bz-H), 7.27 (t, 3J = 7.5 Hz, 1H, Bz-H), 7.11 (t, 3J = 7.5 Hz, 1H, Ar-H), 4.59 (d, 2H, CH2), 3.50 (s br, 2H, S-H); 13C NMR (100 MHz, DMF-d7, 25 °C, ppm): δ = 169.7 (C(O)NH), 140.1, 135.4, 134.2, 132.3, 132.0, 129.0, 128.2, 127.6, 126.1, 125.7 (Ar-C), 43.7 (CH2). Calcd for C14H13NOS2: C, 61.06; H, 4.76; N, 5.09; S, 23.29%. Found: C, 61.11; H, 4.88; N, 4.98; S, 21.96.
Preparation of 3: A sample of [Ti(OPr)₄] (19.9 mg, 0.07 mmol) was added to a solution of H₆-1 (50 mg, 0.07 mmol) and Li₂CO₃ (5 mg, 0.07 mmol) in degassed methanol (20 mL). The mixture was stirred at ambient temperature for 12 h and then filtered. Addition of Ph₄AsCl (61 mg, 0.14 mmol) to the filtrate gave a dark red precipitate, which was isolated by filtration, washed with methanol (2 × 10 mL) and dried in vacuo. Yield 85 mg (0.06 mmol, 80%).

1H NMR (400 MHz, DMF-d₇, 25 °C, ppm): δ = 8.01 (t, 1H, N-H), 7.99–7.81 (m, 40H, As-Ph-H), 7.16 (dd, J = 7.5 Hz, J = 1.5 Hz, 3H, Ar-H), 7.09 (dd, J = 7.5 Hz, J = 1.5 Hz, 3H, Ar-H), 6.76 (t, J = 7.5 Hz, 3H, Ar-H), 4.66 (d, J = 3.8 Hz, 6H, CH₂), 2.47 (s, 9H, CH₃); 13C NMR (100 MHz, DMF-d₇, 25 °C, ppm): δ = 169.4 (C(O)NH), 153.6, 153.4, (C₆H₄S₂-C), 137.1 (C₆Me₃-C), 135.1, 134.2 (AsC₆H₅-C), 134.2 (C₆H₄S₂), 134.1 (C₆Me₃-C), 131.7 (AsC₆H₅-C), 128.7, 122.4 (C₆H₄S₂-C), 122.2 (AsC₆H₅-C), 121.8 (C₆H₄S₂-C), 39.1 (CH₃), 15.7 (CH₃); MS (ESI, negative ions): m/z = 376.7 [Ti(I)]²⁻. Calcd for C₈₁H₆₇N₃As₂O₆S₆Ti: C, 63.98; H, 4.44; N, 2.77; S, 12.63. Found: C, 65.04; H, 4.54; N, 3.39; S, 13.72%.

Complex (Ph₄As)₂[Ti(I)] exhibits a very simple ¹H NMR spectrum, indicating C₃-symmetry of the complex dianions [Ti(I)]²⁻ in solution (Figure S1). The signal for the amide proton is concealed behind the DMF solvent signal at δ = 8.01 ppm and is slightly highfield shifted compared to the resonance observed for the free ligand H₆-1 (N–H resonance at δ = 8.63 ppm). In case of the formation of N–H···S hydrogen bonds, lowfield shift was expected for the amide proton upon complex formation. We ascribe the observed highfield shift to the shielding effect of the bridging aromatic ring.

Figure S1 ¹H NMR spectrum of (Ph₄As)₂[Ti(I)] in DMF-d₇ (*= DMF-, # = acetonitrile-, ^ = water-resonances).
Preparation of 4: The compound was prepared as described for (Ph₄As)₂[Ti(1)] from ligand H₂-2 (50 mg, 0.182 mmol) and Ti(OPr)₄ (17 mg, 0.06 mmol). Yield: 96 mg (0.058 mmol, 97%).

¹H NMR (400 MHz, DMF-d₇, 25 °C, ppm): δ = 9.26 (s, 3H, N-H), 7.98–7.78 (m, 40H, As-Ph-H), 7.94 (dd, 3H, Ph-H), 7.40–7.23 (m, 15H, Bz-H), 7.04 (dd, 3H, Ph-H), 6.70 (t, 3H, Ph-H), 4.58 (d, 6H, CH₂); ¹³C NMR (100 MHz, DMF-d₇, 25 °C, ppm): δ = 169.6 (C(O)NH), 156.3, 150.3, 140.9, 135.1, 134.2, 133.4, 131.7, 129.0, 128.84, 128.80, 127.9, 127.0, 124.7, 121.8 (Ar-C) 43.4 (CH₂); MS (ESI, negative ions): m/z = 433.7 [Ti(2)₃]²⁻. Calcd for C₉₀H₇₃N₃As₂O₃S₆Ti: C, 66.13; H, 4.50; N 2.57; S, 11.77%. Found: C, 66.52; H, 4.54; N, 2.39; S, 10.62.

The proton NMR spectrum of complex (Ph₄As)₂[Ti(2)₃] (Figure S2) is very simple, indicating C₃-symmetry of the complex in solution. The signal for the amide proton is slightly shifted downfield compared to the free ligand H₂-2 (∆δ = 0.19 ppm) and appears at δ = 9.26 ppm.

Figure S2 ¹H NMR spectrum of (Ph₄As)₂[Ti(2)₃] in DMF-d₇ (* = DMF-resonances).
**Preparation of 5:** A sample of [MoCl₄(CH₃CN)₂] (22.4 mg, 0.07 mmol) was added to a solution of H₆-1 (50 mg, 0.07 mmol) and Li₂CO₃ (28 mg, 0.38 mmol) in degassed methanol (20 mL). The mixture was stirred at ambient temperature for 12 h and was then filtered. Addition of Ph₄AsCl·H₂O (61 mg, 0.14 mmol) to the filtrate yielded a dark red precipitate, which was isolated by filtration, washed with methanol (2 × 10 mL) and dried in vacuo.

Yield: 64 mg (0.042 mmol, 60%), C₈₁H₆₇N₃As₂MoO₃S₆ (M = 1568.59 g/mol).

MS (ESI, negative ions): m/z = 802.9 [Mo(I)]⁻, 401.3 [Mo(I)]²⁻; UV-Vis (nm): λ_max = 356, 578.

![Figure S3 UV-Vis spectrum of complex (Ph₄As)₂[Mo(1)] at ambient temperature in DMF.](image)
**Preparation of 6:** A sample of [MoCl₂(CH₃CN)₂] (20.0 mg, 0.06 mmol) was added to a solution of H₂₂ (50 mg, 0.18 mmol) and Na₂CO₃ (19.0 mg, 0.18 mmol) in degassed methanol (20 mL). The solution was stirred under argon at ambient temperature for 12 h and was then filtered. Addition of Ph₄AsCl·H₂O (61 mg, 0.14 mmol) to the filtrate yields a dark red precipitate, which was isolated by filtration, washed with methanol (2 × 10 mL) and dried under vacuum.

Yield: 74 mg (0.04 mmol, 72%), C₉₀H₇₃N₃As₂MoO₃S₆ (M = 1682.73 g/mol). ¹H NMR (400 MHz, DMF- d₇, 25 °C, ppm): δ = 9.58 (t, ³J = 5.7 Hz, 3H, N-H), 7.96 (m, 8H, As-Ph-H), 7.89 (m, 16H, As-Ph-H), 7.85 (m, 16H, As-Ph-H), 7.56 (d, ³J = 7.5 Hz, 6H, Bz-H), 7.56 (s b, 3H, Ar-H), 7.41 (s b, 3H, Ar-H), 7.35 (t, ³J = 7.5 Hz, 6H, Bz-H), 7.22 (t, ³J = 7.5 Hz, 3H, Bz-H), 6.73 (s b, 3H, Ar-H), 4.73 (d, ³J = 5.7 Hz, 6H, CH₂); ¹³C NMR (100 MHz, DMF- d₇, 25 °C, ppm): δ = 169.5 (C(O)NH), 156.9, 151.4 (C₆H₄S₂-C), 141.0, 128.9, 128.0, 127.1 (Bz-C), 135.1, 134.2, 131.7, 122.2 (As-C₆H₅-C), 133.0, 128.94, 123.3, 120.4 (C₆H₄S₂-C), 43.6 (CH₂). MS (ESI, negative ions): m/z = 917.5 [Mo(2)₃]⁻, 458.9 [Mo(2)₃]²⁻; UV-Vis (nm): λ_max = 362 and 580.

![Figure S4](image-url) 
**Figure S4** ¹H NMR spectrum of complex (Ph₄As)₂[Mo(2)₃] at ambient temperature in DMF-d₇.
Aerobic oxidation of complex (Ph₄As)₂[Mo⁴⁺(2)₃] gave the corresponding Mo⁵⁺ species with the associated changes in the electron absorption spectrum (Figure S5, \( \lambda_{\text{max}} = 392, 480, 603 \) and 720 nm).

**Figure S5** UV-Vis spectra of the time dependent aerobic oxidation of (Ph₄As)₂[Mo⁴⁺(2)₃] to (Ph₄As)[Mo⁵⁺(2)₃] in methanol.

**X-ray Data for (Ph₄As)₂[Ti(I)]·3H₂O:** \( \text{C}_{81}\text{H}_{73}\text{N}_3\text{As}_2\text{O}_6\text{S}_6\text{Ti}, \ M = 1574.56, \text{ triclinic,} \ a = 14.433(3), b = 14.456(3), c = 19.842(4) \text{ Å,} \ \alpha = 90.257(4), \ \beta = 90.467(4), \ \gamma = 119.715(4) \ °, \ V = 3595.1(11) \text{ Å}^3, \ T = 153 \text{ K, space group} \ P\bar{1}, \ Z = 2, \ \mu(\text{Mo-K} \alpha) = 1.264 \text{ mm}^{-1}, \ 29245 \text{ intensities measured in the } 2\theta-\text{range } 2.0-25.0°, \ 12643 \text{ unique intensities} (R_{\text{int}} = 0.0663), \ R = 0.0602, \ wR = 0.1241 \text{ for 8757 observed intensities} (I \geq 2\sigma(I)). \text{ Hydrogen atoms were added to the structure model on calculated positions with the exception of the hydrogen atom positions at the three water molecules which were not identified.}
**Computational Studies**

All density functional theory calculations (B3LYP)\(^{[S2]}\) were performed with the Gaussian03 suite of programs,\(^{[S3]}\) using the SDD basis set and pseudopotentials for titanium\(^{[S4]}\) and the D95V\(^{[S5]}\) basis set for all other atoms. The nature of the transition state structures was confirmed by frequency calculations.

**Table S1** Relative energies (in kcal/mol) for the B3LYP/SDD optimized structures of mononuclear tris(benzene-o-dithiolato) molybdenum complexes.

<table>
<thead>
<tr>
<th>complex</th>
<th>pseudo-O(_h)</th>
<th>(D_{3h})</th>
<th>(C_{3h})</th>
<th>triplet state pseudo-O(_h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mo(bdt)}_3]^-)</td>
<td>0</td>
<td>0.70</td>
<td>---(^{[a]})</td>
<td>2.55(^{[b]})</td>
</tr>
<tr>
<td>([\text{Mo(bdt)}_3]^-)</td>
<td>0</td>
<td>---(^{[c]})</td>
<td>5.16</td>
<td>---(^{[d]})</td>
</tr>
<tr>
<td>([\text{Mo(bdt)}_3]^-)</td>
<td>5.37</td>
<td>---(^{[c]})</td>
<td>0</td>
<td>---(^{[d]})</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Optimization of the \(C_{3h}\)-symmetric tris(benzene-o-dithiolato) complex resulted in the \(D_{3h}\)-symmetric isomer; 
\(^{[b]}\) the triplet state is higher in energy; 
\(^{[c]}\) Optimization of the \(D_{3h}\)-symmetric tris(benzene-o-dithiolato) complex resulted in the \(C_{3h}\)-symmetric isomer; 
\(^{[d]}\) no triplet state exists.

**References**


