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Synthesis, structure, and properties of sulfido-bridged dinuclear tungsten(V) complex of dithiolene, $(Pr_4N)_2[W_2(\mu\text{-}S)_2\{S_2C_2(CO_2Et)_2\}_4]$

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Abstract

The reaction of tetrathiotungstate (WS_4^{2-}) with diethyl acetylenedicarboxylate, $EtO_2CC{\equiv}CCO_2Et$, in the presence of dinuclear Pt(III) complex $[Pt_2Cl_2(5\text{-mpyt})_4]$ (5-mpyt = 5-methylpyridine-2-thiolato) as an oxidant gave a sulfido-bridged dinuclear tungsten(V) complex of dithiolene, $(Pr_4N)_2[W_2(\mu\text{-}S)_2\{S_2C_2(CO_2Et)_2\}_4]$ (**1**). The absence of an appropriate oxidant in the reaction system afforded tris(dithiolene) complex $(Pr_4N)_2[W\{S_2C_2(CO_2Et)_2\}_3]$ (**2**). The complex **1** was characterized structurally and spectroscopically. The complex anion in **1** has an edge-shared bioctahedral structure with two bridging sulfide ions, W–W distance being 2.9425(7) Å. The fluxionality of the dithiolene ligand was observed by ^1H-NMR even at −50°C for **1**. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Tungsten; Dithiolene; Tetrathiotungstate; Dinuclear complex; X-ray structure

1. Introduction

High-valent sulfide-bridged dinuclear tungsten and molybdenum complexes usually possess terminally coordinated chalcogenide dianions (O^{2-}, S^{2-}) [1–19]. However, recent progress in the preparation of sulfido-bridged dinuclear tungsten(V) and molybdenum(V) complexes of dithiolenes revealed that the $M(\mu\text{-}S)_2M$ core (M = Mo, W) can be stabilized without terminally coordinated chalcogenide ligands [6,20–22]. Similar structure core with bridging selenide is also seen in the tungsten complex of diselenene [23]. Metal dithiolenes have attracted continuous attention since they were prepared more than 30 years ago [24–26]. Bioinorganic significance of the chemistry of dithiolene complexes containing tungsten and molybdenum has stimulated recent works in this field [20,21]. New methodology for synthesizing metal dithiolene complexes is also under development [27,28].

We have reported that $(Pr_4N)_2WS_4$ reduces trivalent platinum dimer $[Pt_2Cl_2(5\text{-mpyt})_4]$ to divalent dimer $[Pt_2(5\text{-mpyt})_4]$ in CH_3CN while the same reactants produce novel S_4-bridged tetranuclear Pt(III) species $[\{ClPt_2(5\text{-mpyt})_4\}_2S_4]$ in $CHCl_3$ which acts as a weak oxidizing agent [29]. In the former reaction, the final product of the tungsten species was hexatungstate $[W_6O_{19}]^{2-}$. In order to trap the missing sulfur species, diethyl acetylenedicarboxylate was added to the reaction mixture. From that reaction mixture, we unexpectedly isolated dinuclear tungsten complex of dithiolene. We wish to report here the preparation and characterization of sulfido-bridged dinuclear tungsten(V) complex of dithiolene, $(Pr_4N)_2[W_2^V(\mu\text{-}S)_2\{S_2C_2(CO_2Et)_2\}_4]$.

2. Results and discussion

2.1. Preparation

As shown in Scheme 1, the reaction of tetrathiotungstate WS_4^{2-} reduces trivalent platinum dimer

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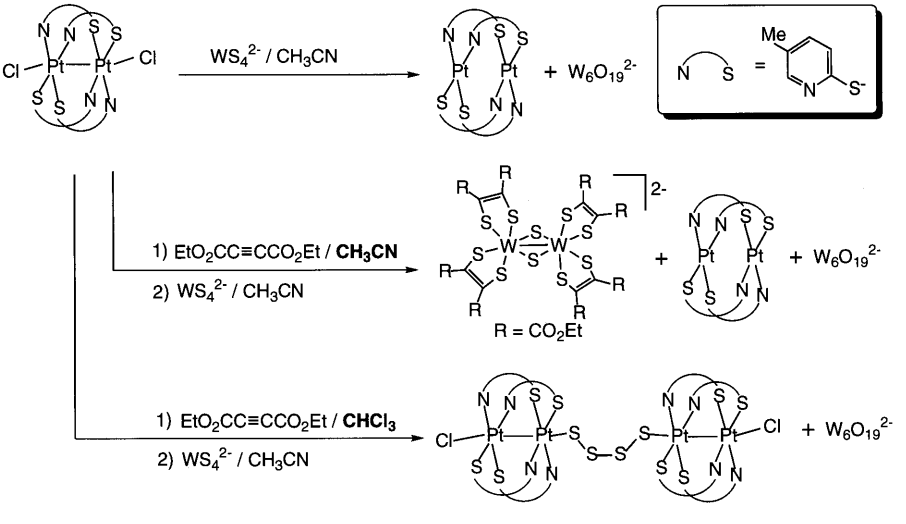
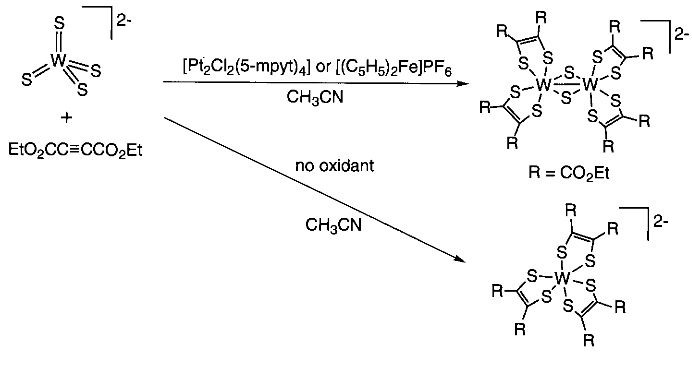


Scheme 1.

$[Pt_2Cl_2(5\text{-mpyt})_4]$ to give divalent species $[Pt_2(5\text{-mpyt})_4]$ and hexatungstate $W_6O_{19}^{2-}$ in CH_3CN [29]. The presence of the diethyl acetylenedicarboxylate, $EtO_2CC\equiv CCO_2Et$, in the reaction system afforded sulfido-bridged dinuclear W(V) dithiolene complex $(Pr_4N)_2[W_2^VS_2\{S_2C_2(CO_2Et)_2\}_4]$ (**1**) in addition to the products from the former reaction. However, we found that the formation of the tetrasulfido-bridged platinum complex prevails over the formation of the dithiolene complex when the reaction was carried out in $CHCl_3$. It indicates that the tetrasulfide ion in $[\{ClPt_2(5\text{-mpyt})_4\}_2S_4]$ does not react with the diethyl acetylenedicarboxylate in $CHCl_3$ and the solvent $CHCl_3$ does not act as an oxidant for the conversion of diethyl acetylenedicarboxylate to dithiolene. No intermediary species such as $[WS\{S_2C_2(CO_2Et)_2\}_2]^{2-}$ were detected, though mononuclear W^{IV} and Mo^{IV} species $[MS(S_2C_2R_2)_2]^{2-}$ have been isolated or proposed as the precursors of dinuclear complex $[M_2S_2(S_2C_2R_2)_4]^{2-}$ [6,20,21].

The reaction of WS_4^{2-} with $EtO_2CC\equiv CCO_2Et$ in the absence of oxidant $[Pt_2Cl_2(5\text{-mpyt})_4]$ was examined to verify whether the oxidant is necessary to obtain the dinuclear W(V) dithiolene complex. Although the UV–vis spectrum of the reaction mixture is indistinguishable from that in the presence of the oxidant, the main reaction products were found to be mononuclear W(IV) species $(Pr_4N)_2[W\{S_2C_2(CO_2Et)_2\}_3]$ (**2**) and $(Pr_4N)_2[W_6O_{19}]$ irrespective of the ratio of WS_4^{2-} and diethyl acetylenedicarboxylate being 1:1 to 1:3 (Scheme 2). The composition of **2** was confirmed by elemental analysis and FABMS. In this reaction, no dinuclear W(V) species were formed. Since the activated acetylene acts as a two-electron reducing agent, the electron balance of WS_4^{2-}–$EtO_2CC\equiv CCO_2Et$ in the reaction should be 1:1 in spite of the mass balance being 1:3. The yield was maximum when the ratio of 1:3 was employed. It is now obvious that the oxidant is necessary for the formation of sulfido-bridged dinuclear W(V) dithiolene complex. Since tris(dithiolene)tungsten(IV) complex shows reversible one-electron oxidation wave in its cyclic voltammogram and the oxidized W(V) species are stable in the time-scale of cyclic voltammetry (vide infra), the formation reaction of **1** may not proceed via tris(dithiolene) complex **2**.

The next question is whether $Pt(III)_2$ species such as $[Pt_2Cl_2(5\text{-mpyt})_4]$ are essential for the formation of sulfido-bridged dinuclear W(V) dithiolene complex or not. The reaction of WS_4^{2-} with $EtO_2CC\equiv CCO_2Et$ in the presence of ferrocenium cation ($[(C_5H_5)_2Fe]PF_6$) as an alternative oxidant was conducted. The UV–vis spectrum and the cyclic voltammogram of the complex obtained from the first eluate clearly showed that the complex is identical with **1**. Thus we concluded that an appropriate oxidant is necessary to form the sulfido-bridged dinuclear W(V) dithiolene complex though $Pt(III)_2$ species are not essential for the formation of it. It is, however, still noteworthy that the use of $[Pt_2Cl_2(5\text{-mpyt})_4]$ as oxidizing agent is more preferable than that of ferrocenium cation since the separation of added



Scheme 2.

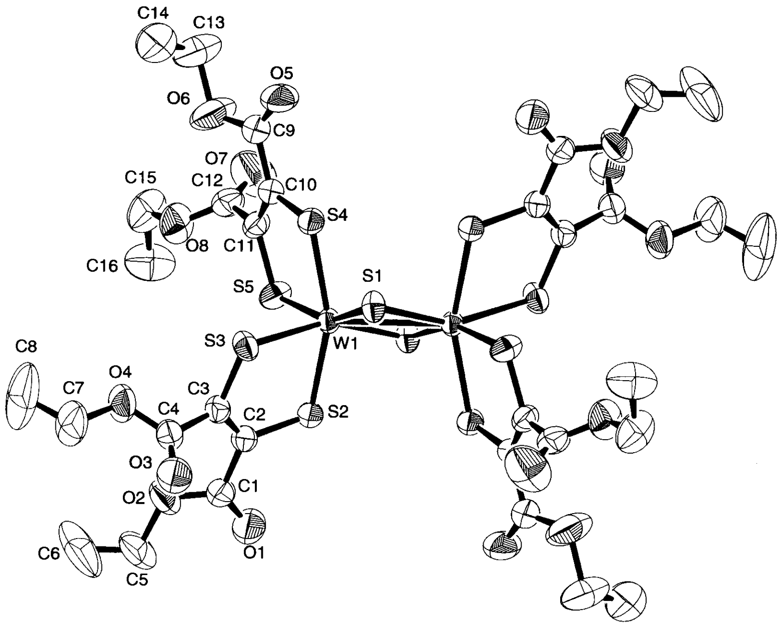


Fig. 1. ORTEP diagram of $[W_2S_2\{S_2C_2(CO_2Et)_2\}_4]^{2-}$ with the atomic numbering scheme showing 50% probability thermal ellipsoids.

oxidant from the reaction mixture is easier owing to the low solubility of reduced species $[Pt_2(5\text{-mpyt})_4]$ in common organic solvents and the reformation of the oxidant from the recovered Pt(II) species is easy [30].

*2.2. Structure of $(Pr_4N)_2[W_2S_2\{S_2C_2(CO_2Et)_2\}_4]$ (**1**)*

Fig. 1 shows the ORTEP drawing of the complex anion in **1**. The anion has an edge-shared bioctahedral structure with two bridging sulfide ions. Each tungsten ion is coordinated by two dithiolene ligands to complete a distorted octahedral coordination sphere. The anion has a crystallographically imposed center of symmetry at the midpoint of W–W single bond. The W–W distance (2.9425(7) Å) is comparable to the metal–metal distances of dithiolene complexes $(Et_4N)_2[W_2S_2(S_2C_2Ph_2)_4]$ (2.9904(6) Å) [20], $(Ph_4P)_2[Mo_2S_2\{S_2C_2(CO_2Me)_2\}_4]$ (2.938(1) Å) [6], and $(Ph_4P)_2[Mo_2S_2(S_2C_2Me_2)_4]$ (3.024(1) Å) [21], where the small difference of metal–metal distances in these complexes can be attributed to the effect of the electron-withdrawing substituents on the dithiolene ligands, and considerably longer than those in the other complexes with $W_2^V(\mu\text{-}S)_2$ core (2.78–2.86 Å) [11–14,16–18,31]. The W–S_{bridge} distances (W1–S1, 2.329(2); W1–S1′, 2.322(2) Å) are normal. The W–S distances to the dithiolene ligands range from 2.384(2) to 2.447(2) Å and are separated into two pairs. The longer pair (W1–S3, 2.445(2); W1–S5, 2.447(2) Å) are *trans* to the W–S_{bridge} bonds and the bonds in shorter pair (W1–S2, 2.396(2), W1–S4, 2.384(2) Å) are *trans* to each other. The C–S bond lengths similarly can be grouped into two pairs with the shorter bonds adjacent to the longer W–S bonds. Similar bond length alternation is commonly observed for the dithiolene complexes with $M_2^V(\mu\text{-}E)_2$ core (M = Mo, W; E = S, Se) [6,20,21,23].

2.3. Spectroscopy

The ^{1}H-NMR spectrum of **1** shows a methyl signal (triplet) and a methylene signal (quartet) assignable to the dithiolene ligand in addition to the signals of tetrapropylammonium cation. The ^{13}C-NMR spectrum of **1** also shows one set of methyl and methylene carbons. Numerical data are listed in the Section 3. The facts that the ^{1}H- and ^{13}C-NMR chemical shifts and the shape of the signals, even at −50°C are essentially identical with those at 20°C, indicate the stereochemical nonrigidity of the dithiolene ligand in the dimer anion. A similar tendency was observed for $[W_2S_2(S_2C_2Ph_2)_4]^{2-}$ [20], $[W_2Se_2\{Se_2C_2(CO_2Me)_2\}_4]^{2-}$ [23] and $[Mo_2S_2\{S_2C_2(CO_2Me)_2\}_4]^{2-}$ [6], where the fluxionality of the dithiolene ligand is claimed. It is noteworthy that the ^{1}H-NMR chemical shifts of **2** are very close to those of **1**.

The UV–vis spectra of **1** and **2** are shown in Fig. 2. The features of their spectra are very similar to those of $[W_2Se_2\{Se_2C_2(COOMe)_2\}_3]^{2-}$ and $[W\{Se_2C_2(COOMe)_2\}_3]^{2-}$, respectively, in which the bands in **1** and **2** are shifted toward shorter wavelength and they are thought to arise from charge transfer [23].

The dimer **1** exhibits an irreversible oxidation wave with $E_{pa} = +0.80$ V and the corresponding irreversible reduction wave with $E_{pc} = +0.24$ V versus Ag/AgCl in CH_3CN. Controlled-potential coulometry for **1** at

+0.90 V gave an electron stoichiometry of 1.93 e W_2^{-1}. Since the cyclic voltammogram of the electrolyzed solution of **1** was different with that of the original complex, the complex **1** is unstable toward oxidation. A reversible one-electron oxidation wave ($E_{1/2} = +0.18$ V vs SCE) and an irreversible oxidation wave ($E_{pa} = +0.39$ V) were observed for $[W_2S_2(S_2C_2Ph_2)_4]^{2-}$ [20]. The oxidation potential of **1** is more positive than that of $[W_2S_2(S_2C_2Ph_2)_4]^{2-}$, indicating the substituent effect on the dithiolene ligand. The tris(dithiolene) complex **2** exhibits a reversible oxidation wave with $E_{1/2} = +0.48$ V ($\Delta E_p = 60$ mV) and an irreversible oxidation wave with $E_{pa} = +0.93$ V in CH_3CN, at the potentials more than 1 V positive compared with the corresponding oxidation potentials of $[W(S_2C_2Ph_2)_3]^{2-}$ [32].

3. Experimental

3.1. Materials

Tetrapropylammonium salt of tetrathiotungstate ($(Pr_4N)_2WS_4$) was prepared by metathesis reaction of tetrapropylammonium bromide and ammonium tetrathiotungstate (Aldrich). Diethyl acetylenedicarboxylate was purchased from Aldrich and used without further purification. Dinuclear platinum(III) complex of 5-methylpyridine-2-thiolate, $[Pt_2Cl_2(5\text{-mpyt})_4]$, was prepared by the literature method [30]. Acetonitrile was dried over calcium hydride and distilled under argon atmosphere. All other commercially available reagents were used as purchased.

3.2. Preparation of $(Pr_4N)_2[W_2S_2\{S_2C_2(CO_2Et)_2\}_4]$ (**1**)

3.2.1. Method 1

An acetonitrile solution (10 ml) of $(Pr_4N)_2WS_4$ (105 mg; 0.15 mmol) was added to a mixture of diethyl acetylenedicarboxylate (51 mg; 0.30 mmol) and $[Pt_2Cl_2(5\text{-mpyt})_4]$ (144 mg; 0.15 mmol) in acetonitrile (150 ml) and stirred for 30 min at 20°C under argon atmosphere. The orange color of the solution containing diethyl acetylenedicarboxylate and Pt(III) complex turned to deep brown immediately after addition of tetrathiotungstate, and the yellow precipitate of Pt(II) dimer gradually separated out from the solution. The precipitate was filtered off and the solution was concentrated to ca. 5 ml under reduced pressure at 20°C. Then the solution was loaded onto an LH-20 column (25 × 2 cm) and eluted with acetonitrile–benzene (10/1) to give several fractions, two of which gave sufficient amount of eluate. The second fraction contained $(Pr_4N)_2[W_6O_{19}]$, as was disclosed by X-ray structural analysis and will be reported elsewhere [33]. The first fraction was concentrated under reduced pressure, and purified again by LH-20 column chromatography at the same conditions. Evaporation of the eluate gave dark brown solid; yield 42 mg (32%). Recrystallization of the product from CH_3CN–MeOH afforded dark brown crystals of X-ray quality.

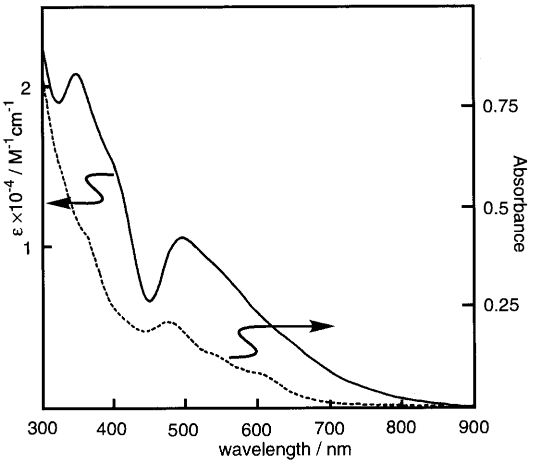


Fig. 2. UV–vis spectra of $[W_2S_2\{S_2C_2(CO_2Et)_2\}_4]^{2-}$ (-----) and $[W\{S_2C_2(CO_2Et)_2\}_3]^{2-}$ (-----) in CH_3CN.

IR (KBr, cm^{-1}): ν(C=O), 1711 (s), 1695 (s); ν(C–O–C), 1236 (vs).

UV–vis (CH_3CN, nm): 348 (ε 20 200 M^{-1} cm^{-1}), 390 sh (ca. 15 800), 494 (10 700).

^{1}H-NMR (CD_3CN, ppm): δ 0.93 (t, 3H, Pr_4N^+), 1.24 (t, 3H, CH_3CH_2O–), 1.62 (m, 2H, Pr_4N^+), 3.01 (m, 2H, Pr_4N^+), 4.16 (q, 2H, CH_3CH_2O–).

^{13}C-NMR (CD_3CN, ppm): δ 10.86 (Pr_4N^+), 14.48 (CH_3CH_2O–), 16.11 (Pr_4N^+), 61.14 (Pr_4N^+), 62.31 (CH_3CH_2O–), 151.21 (C=C), 166.97 (–COO–).

Anal. Calc. for $C_{56}H_{96}N_2O_{16}S_{10}W_2$: C, 38.62; H, 5.56; N, 1.61; S, 18.41. Found: C, 38.22; H, 5.36; N, 1.58; S, 18.19%.

3.2.1.1. Crystal data for **1**.

$C_{56}H_{96}N_2O_{16}S_{10}W_2$, FW = 1741.68, dark brown, rhombic, size 0.35 × 0.25 × 0.18 mm^3, monoclinic, space group $P2_1/n$ (#14), $a = 14.333(3)$, $b = 17.014(4)$, $c = 16.214(3)$ Å, $\beta = 110.92(1)°$, $V = 3693(1)$ Å^3, $T = 23°C$, $Z = 2$, $D_{calc} = 1.57$ g cm^{-3}, $\mu(\text{Mo–K}_\alpha) = 34.6$ cm^{-1}, psi-scan, $trans_{min}$: 0.715, $trans_{max}$: 1.00, 11 112 reflections measured in the range $2.57 \le \theta \le 30.01°$, 10 770 unique reflections ($R_{int} = 0.030$), 6653 observed reflections with $I > 2\sigma(I)$, 388 parameters, $R_1 = 0.047$, $R_w = 0.063$, Goodness-of-fit = 1.07, largest difference peak and hole: 1.54, −0.64 e Å^{-3}.

3.2.2. Method 2

An acetonitrile solution (15 ml) of $(Pr_4N)_2WS_4$ (90 mg; 0.13 mmol) was added to a mixture of diethyl acetylenedicarboxylate (45 mg; 0.26 mmol) and $[(C_5H_5)_2Fe]PF_6$ (87 mg; 0.26 mmol) in acetonitrile (55 ml) and stirred for 30 min at 20°C under argon atmosphere. The deep blue solution containing diethyl

Table 1
Selected bond lengths (Å) and angles (°) for $(Pr_4N)_2[W_2S_2\{S_2C_2(CO_2Et)_2\}_4]$ (**1**)

Bond lengths			
W1–W1	2.9425(7)	S2–C2	1.750(8)
W1–S1	2.329(2)	S3–C3	1.716(8)
W1–S1′	2.322(2)	S4–C10	1.736(8)
W1–S2	2.396(2)	S5–C11	1.703(7)
W1–S3	2.445(2)	C2–C3	1.35(1)
W1–S4	2.384(2)	C10–C11	1.36(1)
W1–S5	2.447(2)		
Bond angles			
S1–W1–S1′	101.49(6)	S1′–W1–S5	87.08(7)
S1–W1–S3	83.67(7)	S1–W1–S5	157.39(7)
S2–W1–S3	79.97(6)	S2–W1–S4	157.21(7)
S3–W1–S5	97.04(8)	S1′–W1–S3	155.94(7)
S4–W1–S5	79.62(6)	W1–S1–W1′	78.51(6)

acetylenedicarboxylate and ferrocenium hexafluorophosphate turned to deep brown immediately after addition of tetrathiotungstate. A small amount of yellow–brown precipitate was filtered off and the solution was concentrated to ca. 5 ml under reduced pressure at 20°C. Then the solution was loaded onto an LH-20 column (25 × 2 cm) and eluted with 5:1 acetonitrile–benzene. Similarly to the method 1, the first fraction (less distinct than that of the method 1) was concentrated under reduced pressure, and purified again by LH-20 column chromatography. Evaporation of the eluate gave dark brown solid; yield 30 mg (26%).

3.3. Preparation of $(Pr_4N)_2[W\{S_2C_2(CO_2Et)_2\}_3]$ (2)

The procedure for this complex is very similar to that for **1** with the exception that the ratio of WS_4^{2-} and diethyl acetylenedicarboxylate was 1:3 and no oxidizing agent was used. An acetonitrile solution (10 ml) of $(Pr_4N)_2WS_4$ (123 mg; 0.18 mmol) was added to an acetonitrile solution (70 ml) of diethyl acetylenedicarboxylate (92 mg; 0.54 mmol) and stirred for 10 min at 20°C under argon atmosphere. The deep brown solution was concentrated to ca. 5 ml under reduced pressure at 20°C. Similar work-up to the method 1 for the preparation of **1** afforded deep brown solid; yield 41 mg (18%). IR (KBr, cm^{-1}): ν(C=O), 1715 (s), 1687 (s); ν(C–O–C), 1228 (vs). UV–vis (CH_3CN, nm): 360 sh, 474, 548 sh, 602 sh. FABMS: m/z 1258 [M^+]. ^{1}H-NMR (CD_3CN, ppm): δ 0.93 (t, 3H, Pr_4N^+), 1.24 (t, 3H, CH_3CH_2O–), 1.61 (m, 2H, Pr_4N^+), 3.00 (m, 2H, Pr_4N^+), 4.13 (q, 2H, CH_3CH_2O–). Anal. Calc. for $C_{48}H_{86}N_2O_{12}S_6W$: C, 45.78; H, 6.88; N, 2.22; S, 15.27. Found: C, 45.54; H, 7.01; N, 2.32; S, 15.52%.

3.4. X-ray structural determinations

Crystals of **1** suitable for X-ray structural analysis were obtained by recrystallization from CH_3CN–MeOH. The crystal was sealed in a thin-walled glass capillary. Intensity data were collected on a Rigaku AFC-5R diffractometer using graphite-monochromated Mo–K_α ($\lambda = 0.71069$ Å) radiation at 298 K. The unit cell parameters were obtained by least-squares refinement of 25 reflections ($25 \leq 2\theta \leq 30°$). The intensities of three standard reflections, monitored after every 150 reflections, showed no appreciable decay during the data collection. The data were corrected for Lorentz and polarization effects. An empirical absorption correction based on azimuthal scans of three reflections was applied [34].

The crystal structure was solved by heavy-atom method by using DIRDIF [35]. The positional and thermal parameters of non-H atoms were refined anisotropically by the full-matrix least-squares method. The minimized function was $\Sigma w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + p|F_o|^2$ ($p = 1.64 \times 10^{-3}$). No attempt was made to locate hydrogen atoms in the structure analysis. In the final cycle of the refinement, parameter shifts were less than 0.1σ. No correction was made for secondary extinction.

All calculations were performed using TEXSAN [36]. Listings of the selected bond distances and angles are summarized in Table 1.

3.5. Other measurements

UV–vis spectra were recorded on a Shimadzu UV-1600 spectrophotometer at 20°C. IR spectra were recorded on a Jasco FTIR-420 infrared spectrophotometer. The ^{1}H- and ^{13}C-NMR spectra were obtained at 400 and 100.5 MHz, respectively, with a JEOL JNM-GX400 spectrometer. Cyclic voltammetry was performed with a Hokuto HA-301 potentiostat and a Hokuto HB-104 function generator equipped with a Yokokawa 3086 X–Y recorder. The working and the counter electrodes were a platinum disk and a platinum wire, respectively. Cyclic voltammograms were recorded at a scan rate of 50 mV s^{-1}. The sample solutions (ca. 0.5 mM) in 0.1 M TBAP–acetonitrile were deoxygenated with a stream of argon. The reference electrode was Ag/AgCl and the half-wave potential of Fc^+/Fc ($E_{1/2}(Fc^{+/0})$ versus Ag/AgCl) was +0.44 V. Controlled-potential coulometry was carried out in 0.1 M TBAP–acetonitrile with a standard H-type cell with a Hokuto HA-310 potentiostat and a Fuso Model 1119 integrator. The working electrode was made of platinum gauze, and the working compartment was separated from the counter compartment by a sintered-glass disk.

4. Supplementary data

Complete lists of bond lengths and angles and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre CCDC no. 142096. Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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