Inorganica Chimica Acta, *177* (1990) 239–246

Reactivity of the metal(0) dithiocarbamato carbonyl complex $[M(CO)_4(S_2CNEt_2)]^-$ (M=Mo, W): synthesis, structure and cyclic voltammetry of the tungsten(0) dithiocarbamato carbonyl complex and a new mixed-valence dinuclear tungsten–sulfur compound $[Et_4N]_2[(OC)_4WS_2WS_2]$

Botao Zhuang*, Peihua Yu, Liangren Huang, Lingjie He and Jiaxi Lu

Fujian Institute of Research on the Structure of Matter, Fuzhou Research Laboratory of Structural Chemistry, Chinese Academy of Sciences, Fuzhou, Fujian 350002 (China)

(Received April 5, 1990; revised July 3, 1990)

Abstract

The reaction of tungsten hexacarbonyl with tetraethylammonium diethyldithiocarbamate in MeCN affords the tungsten(0) dithiocarbamato complex $[Et_4N][W(CO)_4(S_2CNEt_2)]$ (**1**) and **1** reacts with tetraethylammonium tungsten tetrathiolate $[Et_4N]_2WS_4$ in warm MeCN (or MeOH) resulting in a new mixed-valence dinuclear tungsten–sulfur compound $[Et_4N]_2[(OC)_4WS_2WS_2]$ (**2**). **1** and **2** were characterized by routine elemental analysis and IR spectroscopy, and their structures were determined from three-dimensional X-ray data. **1** crystallizes in the orthorhombic space group $Pca2_1$ with $a = 19.516(2)$, $b = 8.147(1)$, $c = 14.338(1)$ Å; $V = 2279.8$ Å^3; $Z = 4$ $D_c = 1.83$ g/cm^3; $R = 0.046$, $R_w = 0.053$ for 1766 independent reflections ($I > 3\sigma(I)$). **2** crystallizes in the orthorhombic space group $Pbcm$ with $a = 18.414(4)$, $b = 12.007(2)$, $c = 13.523(3)$ Å; $V = 2989.7$ Å^3; $Z = 4$; $D_c = 1.93$ g/cm^3; $R = 0.050$, $R_w = 0.055$ for 2373 independent reflections ($I > 3\sigma(I)$). The structure of **1** is similar to the Mo analog, $[Mo(CO)_4(S_2CNEt_2)]^-$, with W–S of 2.591(3) and 2.636(4) Å and the structure of the anion of **2** consist of an octahedron around a low-valence tungsten atom and a tetrahedron with a high-valence tungsten atom in the center sharing an edge which is the line between the two bridged sulfur atoms. The W–W bond length is 3.0104(6) Å and the bimetallic center WS_2W is in a plane with WSW angles of 77.9(1) and 77.9(1)°. Cyclic voltammetry of **1** and **2** is presented and a CV study of **2** shows the electrochemistry on the two metal centers with different valences is different. Like another member of this family, $[(OC)_4MoS_2WS_2]^{2-}$, the existence of $W \rightarrow WS_4$ electron delocalization in **2** is discussed.

Introduction

As a part of studies [1–4] on molybdenum–sulfur complexes with molybdenum in a low oxidation state the investigation on introducing molybdenum (tungsten) atoms in a low oxidation state into the cluster compounds containing Mo(W)–S bonds and building the mixed-metal and mixed-valence metal cluster, which will be interesting from a structural point of view and will possess unusual electronic properties and available reactivities, has led to our discovery of a new Mo(W)–S cluster compound family $\{(CO)_4M']_nMS_4\}^{2-}$ (M′ = Mo, W; M = Mo, W; $n = 1$, 2) [5] which corresponds to the Mo–Fe–S linear clusters $[(FeX_2)_nMS_4]^{2-}$ (X = Cl, SR; $n = 1$, 2; M = Mo, W) [6] that have been studied as model compounds of the active center of nitrogenase. In a previous publication, we presented a dinuclear mixed metal Mo–W–S compound member $[(OC)_4MoWS_4]^{2-}$ [5]. Herein we report the new dinuclear mixed-valence W–S compound member $[(OC)_4WS_2WS_2]^{2-}$. Also the synthesis and structure of the new tungsten(0) dithiocarbamato carbonyl as the starting material in the synthetic reaction is discussed.

Experimental

Materials and methods

Tungsten hexacarbonyl was purchased from Alfa. Acetonitrile was distilled from CaH_2. Methanol and isopropanol were dried by distillation with magnesium

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*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

methoxide. Sodium diethyldithiocarbamate was purchased from the Shanghai Chemical Reagent Company in China. Tetraethylammonium tetrathiotungstate $[Et_4N]_2WS_4$ was prepared by literature methods [7]. All synthetic reaction procedures, crystal growth and preparation of the sample for X-ray determination and cyclic voltammetry were carried out under nitrogen atmosphere using the Schlenk technique and degassed solvents. All reactants were also degassed before use.

Instrumentation

Perkin-Elmer 577 infrared spectrometer; Enraf Nonius CAD4 diffractometer; CARLO ERBA Strumentation elemental analyzer-MOD 1106, CV-1B from BAS (Bioanalytical Systems).

Synthesis of $[Et_4N]_2[W(CO)_4(S_2CNEt_2)]$ (1)

A mixture of solid $NaS_2CNEt_2 \cdot 3H_2O$ (5.65 g, 25 mmol) and Et_4NCl (4.15 g, 25 mmol) in 150 ml MeCN was stirred at 55 °C for 4 h and then was filtered onto solid $W(CO)_6$ (8.8 g, 25 mmol). The resulting reaction mixture was refluxed at 82 °C for 24 h resulting in a red–brown solution. After cooling to room temperature it was evaporated to 50 ml by vacuum. To the concentrated solution was added 100 ml isopropanol, and 4.67 g of the yellow solid product **1** was obtained by filtering, washing with isopropanol and hexane, and drying *in vacuo*. *Anal.* Calc. for $C_{17}H_{20}N_2O_4S_2W$: C, 35.54; H, 5.23; N, 4.88. Found: C, 35.34; H, 5.43; N, 5.06%. IR (KBr, pellet) 1980(s), 1850(s), 1825(s) and 1775(s) cm^{-1} (νWC=O). Another 3.12 g of a crystalline product, which is identical with **1**, were collected from the filtrate by cooling at 4 °C for several hours. The total yield is 54.5%.

Synthesis of $[Et_4N][(OC)_4WS_2WS_2]$ (2) and synthetic reaction with variation of reaction conditions

(a) 0.58 g (1 mmol) of $[Et_4N]_2WS_4$ was reacted with 1.15 g (2 mmol) of $[Et_4N]W(CO)_4(S_2CNEt_2)$ in a mixed solvent of 15 ml MeCN and 50 ml EtOH at 70–75 °C for 3 days. After cooling to room temperature the dark reaction mixture was filtered and the deep red filtrate was cooled at 4 °C for 2 days. A total of 0.38 g of the red crystalline product **2** was collected by filtering, washing with EtOH and

TABLE 1. Crystallographic data and data collection parameters for $[Et_4N][W(CO)_4(S_2CNEt_2)]$ (1) and $[Et_4N]_2[W_2S_4(CO)_4]$ (2)

	1	**2**
Formula	$C_{17}H_{30}N_2O_4S_2W$	$C_{20}H_{40}N_2O_4S_4W_2$
Molecular weight	574.42	868.51
a (Å)	19.516(2)	18.414(4)
b (Å)	8.147(1)	12.007(2)
c (Å)	14.338(1)	13.523(3)
Crystal system	orthorhombic	orthorhombic
V (Å^3)	2279.8	2989.7
D_{calc} (g/cm^3)	1.83	1.93
Z	4	4
Space group	$Pca2_1$ (No. 29)	$Pbcm$ (No. 57)
Crystal dimensions (mm)	0.12×0.40×0.50	0.03×0.35×0.35
Radiation	Mo Kα (λ=0.71073 Å)	Mo Kα (λ=0.71073 Å)
Absorption coefficient, μ (cm^{-1})	58.9	81.5
Scan mode	ω–2θ	ω–2θ
Data collected	$2\theta_{max}=52°$ $(+h-k-l)$	$2\theta_{max}=52°$ $(+h+k+l)$
Unique data	2437	3319
Data used in refinement, $I>3\sigma(I)$	1766	2373
Corrections	LP factor anisotropic decay (0.983–1.020) empirical absorption (DIFABS 0.961–1.006)	LP factor anisotropic decay (0.982–1.021) empirical absorption (DIFABS 0.872–1.035)
Phasing technique	direct methods	direct methods
No. non-hydrogen atoms in asymmetric unit	23	23
No. variables	234	177
R[a]	0.046	0.050
R_w[b]	0.053	0.055

[a] $R=\Sigma|F_o|-|F_c||/\Sigma|F_o|$. [b] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

drying *in vacuo*, yield 44% (based on $[Et_4N]_2WS_4$ used). *Anal.* Calc. for $C_{20}H_{40}N_2O_4S_4W$: C, 27.65; H, 4.61; N, 3.23; S, 14.75. Found C, 28.20; H, 4.18; N, 3.47; S, 15.01%. IR (KBr pellet) 2004(s), 1872(s), 1850(s), 1825(s), 1810(sh) (νWC=O); 476(s), 470(s) (νW–St) cm^{-1}.

(b) A mixture of 1.10 g (1.92 mmol) of $[Et_4N]_2WS_4$ and 1.10 g (1.92 mmol) of $[Et_4N]W(CO)_4(S_2CNEt_2)$ in 40 ml MeCN was stirred at 45–50 °C for 40 h, then cooled to room temperature and evaporated to 20 ml *in vacuo*. The resulting reaction mixture was filtered to remove a small amount of yellow precipitate. To the concentrated filtrate was added 45 ml EtOH and a red crystalline product formed. A total of 0.41 g of this red crystalline product **2** was obtained by filtering, washing with EtOH and drying *in vacuo*. From the filtrate another 0.08 g of **2** was collected by cooling at 4 °C for 2 days. The total yield is 29.4%.

(c) A mixture of 0.57 g of $[Et_4N]_2WS_4$ (1 mmol) and 0.58 g of $[Et_4N]W(CO)_4(S_2CNEt_2)$ (1 mmol) in 50 ml MeOH was stirred at 55–60 °C for 24 h. A total of 0.13 g of the red–brown solid product **3** was obtained by cooling to room temperature, filtering, washing with MeOH and drying *in vacuo*. *Anal.* Calc. for $C_{24}H_{40}N_2O_8S_4W_3$: C, 24.74; H, 3.44; N, 2.41; S, 10.99; Found: C, 23.47; H, 3.58; N, 2.87; S, 10.98%. IR (KBr pellet) 2000(s), 1876(s), 1860(s), 1818(s) (νWC=O), 460(m), 428, 424(s) (νW–Sb) cm^{-1}. Taking into account the absence of νW–St (476, 470) in the IR spectra of **3** and the elemental analysis data, it is beyond any doubt that product **3** is a linear trinuclear tungsten–sulfur compound $[Et_4N]_2[(OC)_4WS_2WS_2W(CO)_4]$ (**3**) (yield 22% based on $[Et_4N][W(CO)_4(S_2CNEt_2)]$ used). The resulting filtrate was cooled at 4 °C overnight and 0.09 g of the red crystalline product **2** was obtained by filtering, washing and drying *in vacuo*.

(d) 0.5 g of $[Et_4N]_2WS_4$ (0.87 mmol) was reacted with 1.3 g of $[Et_4N]W(CO)_4(S_2CNEt_2)$ (2.26 mmol) in 60 ml MeOH at 60–65 °C for 3 days. 0.5 g of **3** (yield 50%) and 0.04 g of **2** were isolated by the same isolation procedure as for reaction (c).

X-ray structure determination

The X-ray crystallographic experiments were performed on an Enraf-Nonius CAD4 computer controlled Kappa diffractometer utilizing graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. All crystallographic computations were carried out with the SDP/VAX (Enraf-Nonius and B. A. Frenz and associates, Inc.) on a VAX computer. Crystal data and experimental conditions are given in Table 1.

The crystal was mounted on a glass fiber with epoxy cement. The intensities were collected in the range of $2 < 2\theta < 52°$ using ω–2θ scan mode. Lorentz and polarization corrections were applied to the data and the empirical absorption using the program DIFABS was made. The structures were solved by direct methods. The W and S atoms (a total of 3 for **1** and a total of 5 for **2**) were located at first and the remaining atoms were located in succeeding difference Fourier synthesis. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined for **1**. For **2**, hydrogen atoms were not included in the calculation. The structures were refined by full-matrix least-squares and the final cycle of refinement included 234 for **1** and 177 for **2** variable parameters and converged (largest parameter shifts were 0.33σ (for **1**) and 0.13σ (for **2**)) with R of 0.046 and 0.050 and R_w of 0.053 and 0.055 for **1** and **2**, respectively. The e.s.d. of observations of unit weight are 1.57 and 2.14 for **1** and **2**, respectively. The highest peaks in the final difference Fourier are 0.88 and 1.13 e/Å^3 for **1** and **2**, respectively. The final positional and thermal parameters with estimated standard deviations are listed in Tables 2 and 3.

TABLE 2. Positional parameters and their e.s.d.s. for $[Et_4N][W(CO)_4(S_2CNEt_2)]$ (**1**)

Atom	x	y	z	B (Å^2)
W	0.16205(2)	0.38614(7)	0.4975(0)	3.133(9)
S(1)	0.0508(2)	0.5593(5)	0.4915(5)	3.51(7)
S(2)	0.0970(2)	0.3618(6)	0.3370(3)	3.78(9)
C(1)	0.2357(7)	0.234(2)	0.469(1)	3.7(4)
C(2)	0.2008(8)	0.439(3)	0.615(1)	4.2(4)
C(3)	0.1090(7)	0.203(2)	0.548(1)	3.9(4)
C(4)	0.2252(7)	0.557(2)	0.439(1)	3.7(4)
O(1)	0.2796(6)	0.144(2)	0.453(1)	6.5(4)
O(2)	0.2227(7)	0.464(2)	0.688(1)	8.0(5)
O(3)	0.0807(7)	0.093(2)	0.578(1)	6.4(4)
O(4)	0.2663(6)	0.651(2)	0.411(1)	6.3(4)
N(1)	−0.0226(6)	0.523(2)	0.3337(9)	3.4(3)
C(10)	0.0335(7)	0.489(2)	0.381(1)	2.8(3)
C(11)	−0.0768(8)	0.630(2)	0.371(1)	3.5(4)
C(12)	−0.0682(9)	0.797(3)	0.336(2)	6.1(5)
C(13)	−0.0364(8)	0.451(3)	0.241(1)	4.5(4)
C(14)	−0.0752(9)	0.282(3)	0.250(2)	6.9(6)
N(2)	0.8541(6)	0.088(2)	0.684(1)	3.3(3)
C(21)	0.9224(8)	0.002(2)	0.670(1)	4.0(4)
C(22)	0.924(1)	−0.105(3)	0.585(2)	8.3(6)
C(23)	0.7968(7)	−0.040(2)	0.692(1)	3.6(4)
C(24)	0.7277(8)	0.031(3)	0.716(2)	5.9(5)
C(25)	0.8599(8)	0.194(2)	0.772(1)	4.1(4)
C(26)	0.866(1)	0.094(3)	0.860(2)	6.3(6)
C(27)	0.8358(9)	0.204(3)	0.601(2)	5.5(5)
C(28)	0.891(1)	0.315(3)	0.575(2)	9.3(7)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

TABLE 3. Positional parameters and their e.s.d.s. for $[Et_4N]_2[(OC)_4WS_2WS_2]$ (**2**)

Atom	x	y	z	B (Å^2)
W(1)	−0.30516(4)	0.05096(5)	0.2500(0)	3.16(1)
W(2)	0.18799(4)	−0.12387(5)	0.2500(0)	3.36(1)
S(1)	0.1859(2)	0.0869(3)	0.2500(0)	3.45(8)
S(2)	0.3258(3)	−0.1326(4)	0.2500(0)	5.5(1)
S(3)	0.3526(2)	0.1235(3)	0.1188(3)	5.88(9)
O(1)	0.1789(8)	−0.384(1)	0.2500(0)	6.3(4)
O(2)	0.0197(7)	−0.097(1)	0.2500(0)	6.0(3)
O(3)	0.1859(6)	−0.1232(8)	0.0150(7)	7.1(3)
C(1)	0.183(1)	−0.283(1)	0.2500(0)	4.5(4)
C(2)	0.0829(9)	−0.111(1)	0.2500(0)	3.9(4)
C(3)	0.1907(7)	−0.124(1)	0.100(1)	4.8(3)
N(1)	0.4185(7)	0.487(1)	0.2500(0)	3.7(3)
C(11)	0.427(1)	0.591(2)	0.319(2)	4.3(5)
C(11′)	0.489(1)	0.013(2)	0.806(2)	4.3(5)
C(12)	0.3543(9)	0.592(1)	0.387(1)	7.4(4)
C(13)	0.414(1)	0.377(2)	0.318(2)	4.9(5)
C(13′)	0.349(1)	0.014(2)	0.694(2)	4.6(5)
C(14)	0.4860(9)	0.375(1)	0.383(1)	7.2(4)
N(2)	0.0945(8)	0.2500(0)	0.5000(0)	4.0(3)
C(21)	0.1418(9)	0.356(1)	0.491(1)	6.3(4)
C(22)	0.1917(9)	0.353(1)	0.401(1)	7.9(4)
C(23)	0.0498(7)	0.262(1)	0.593(1)	6.1(3)
C(24)	−0.005(1)	0.360(2)	0.586(1)	9.0(5)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1)+b^2\beta(1,1)+b^2\beta(2,2)+c^2\beta(3,3)+ab(\cos\gamma)\beta(1,2)+ac(\cos\beta)\beta(1,3)+bc(\cos\alpha)\beta(2,3)]$.

Electrochemical measurements

Cyclic voltammetry (CV) experiments were carried out with a three electrode cell using 0.1 M Bu_4NBF_4 as the supporting electrolyte and MeCN as solvent. The working electrode was glassy carbon and the reference electrode was an aqueous SCE separated from the sample solution by a salt bridge. Solutions were deoxygenated and blanketed with nitrogen.

Results and discussion

Synthesis of $[Et_4N][W(CO)_4(S_2CNEt_2)]$ (1) and $[Et_4N]_2[(OC)_4WS_2WS_2]$ (2)

Similar to the synthesis of the Mo analog $[Mo(CO)_4(S_2CNEt_2)]^{2-}$ [8] the tungsten(0) dithiocarbamato complex $[Et_4N][W(CO)_4(S_2CNEt_2)]$ (**1**) was prepared in high yield by the reaction of tetraethylammonium dithiocarbamate in acetonitrile, but a higher reaction temperature (at 82 °C) is necessary for obtaining good yield. This is consistent with the general fact that the tungsten compounds are more inert to reactions than the molybdenum compounds [9].

By the same action as the Mo analog, $[Mo(CO)_4(S_2CNEt_2)]^-$ [8], reaction of one equiv. of $[Et_4N][W(CO)_4(S_2CNEt_2)]$ (**1**) with $[Et_4N]_2WS_4$ in warm acetonitrile or methanol affords a new mixed-valence dinuclear tungsten–sulfur compound, $[Et_4N]_2[(CO)_4WS_2WS_2]$ (**2**), via a substitution of the $S_2CNEt_2^-$ ligand by the bidentate ligand WS_4^{2-} according to eqn. (1)

$$[Et_4N]_2[WS_4]^- + [Et_4N][M(CO)_4(S_2CNEt_2)] \xrightarrow[\text{warm}]{\text{MeCN or MeOH}}$$

$$[Et_4N]_2[(OC)_4MS_2WS_2] + [S_2CNEt_2]^- + [Et_4N]^+ \qquad (1)$$

M = Mo, W

Reaction conditions, in particular the solvent used, obviously influence the formation of the product. As is shown in Table 4 a higher reaction temperature will raise the yield and different solvents used lead to the formation of different types of products. The main product **3** and a small amount of **2** will be isolated when MeOH is used as the solvent in the preparative reaction and only product **2** can be obtained when the preparative reaction. is carried out in MeCN no matter what ratio of reactants is employed. These results not only imply the existence of dissociation of the trinuclear product **3** into dinuclear product **2** in MeCN following equilibrium (2)

$$[Et_4N]_2[(OC)_4MS_2WS_2M(CO)_4] + Et_4N^+ + [S_2CNEt_2]^- \rightleftharpoons$$

$$[Et_4N]_2[(OC)_4MS_2WS_2] + [M(CO)_4(S_2CNEt_2)]^- + Et_4N^+ \qquad (2)$$

M = Mo [5], W

which was pointed out for the Mo–W analog $[(OC)_4MoS_2WS_2]^{2-}$ in the previous paper [5], but also indicate that $[(OC)_4WS_2WS_2]^{2-}$ is so reactive that the reactions of $[(OC)_4WS_2WS_2]^{2-}$ with $W(CO)_4(S_2CNEt_2)^-$ and WS_4^{2-} with $[W(CO)_4(S_2CNEt_2)]^-$ take place simultaneously in the synthetic reaction system. This is the reason why trinuclear **3** can be isolated as the main product from the synthetic reaction in MeOH even if a 1:1 ratio of WS_4^{2-} to $W(CO)_4(S_2CNEt_2)^-$ is employed. This synthetic reaction also provides an example and evidence for the similarity of the new Mo–W–S complex family $\{[M(CO)_4]_nM'S_4\}^{2-}$ to the linear Fe–Mo–S clusters $[(FeX_2)_nMS_4]^{2-}$ [16].

TABLE 4. The influence of reaction conditions on the formation and yield of product

Ratio of reactants $[W(CO)_4(dtc)]^-:WS_4^{2-}$	Temperature (°C)	Solvent	Product (%)
2.5:1	60–65	MeOH	**3**(50)
1:1	55–60	MeOH	**3**(25)
2:1	70–75	MeCN	**2**(44)
1:1	45–50	MeCN	**2**(29)

It is worth noting that $[M(CO)_4(S_2CNEt_2)]^-$ (M = Mo, W) seems to provide only the $M(CO)_4$ moiety in the synthesis of the series of $[(OC)_4M]_nM'S_4]^{2-}$, but it is possible to introduce a variety of the $Mo(CO)_n(S_2CNEt_2)$ moiety ($n < 4$) if $M(CO)_4(S_2CNEt_2)^-$ undergoes certain oxidation during the synthetic reaction for the oxidation of $[Mo(CO)_4(S_2CNEt_2)]^-$ is able to afford $[Mo(CO)_2(S_2CNEt_2)_2]$ in which the oxidation state of Mo atom is +II [8].

Structure of $[Et_4N][W(CO)_4(S_2CNEt_2)]$ (1) and $[Et_4N]_2[(OC)_4WS_2WS_2]$ (2)

The bond distances and bond angles of **1** and **2** are listed in Tables 5 and 6, respectively, and the molecular structures of the anions of **1** and **2** are depicted in Figs. 1 and 2, respectively. **1** consists of the cation, Et_4N^+, and anion, $[W(CO)_4(S_2CNEt_2)]^-$. The geometry around the W atom in the anion of **1** is a distorted octahedron with a small SWS angle of 66.9(2)° and the structure of the anion of **1** possesses a C_2 non-crystallographic axis through W, C(10) and N atoms and thus becomes pseudo-C_{2v} symmetry. The W–S bond distances of 2.591(3) and 2.636(5) Å are comparable with that observed in the dinuclear W(0)–SR compound $[W_2(CO)_8(SPh)_2]^{2-}$ (2.590 Å) [10]. It is obvious that the structural configuration of the anion of **1** is basically the same as that of the Mo analog, $[Mo(CO)_4(S_2CNEt_2)]^-$ [8], so that **1** exhibits a reactivity similar to that of the Mo analog. **2** is composed of two discrete cations, Et_4N^+, and one dinuclear anion, $[(OC)_4WS_2WS_2]^{2-}$. As shown in Fig. 2, in the anion of **2**, there are two tungsten atoms W(1) and W(2) in two different coordination environments. The W(1) atom is located at the center of a tetrahedron composed of two terminal sulfur atoms and two bridging sulfur atoms and the geometry around the W(2) atom is an octahedron comprising four carbon atoms from the terminal carbonyls and two bridging sulfur atoms. Similar to the configuration of the anion $[(CO)_4MoS_2WS_2]^{2-}$ [5], the whole anion of **2** could be considered to be a structure which consists of an octahedron and a tetrahedron sharing an edge possessing a symmetric mirror with two W atoms, two bridging S and two C atoms from the terminal carbonyls *trans* to the bridging S on it, and a pseudo-C_2 through the two W atoms. The W–W bond distance and WSW angle are 3.0103(7) Å and 77.9(1)°, respectively, indicating a weak metal–metal interaction. The $W(1)-S_t$ bond distance of 2.161(3) Å is a little bit longer than that in the Fe–W–S compound, $[(S_5)FeS_2WS_2]^{2-}$ (2.16 Å) [11], $[S_2WS_2FeS_2WS_2]^{3-}$ (2.166 Å) [12], $[(PhS)_2FeS_2WS_2]^{2-}$ (2.157 Å) [13] and the Mo–W–S compound $[Mo(CO)_4S_2WS_2]^{2-}$ (2.154 Å) [5], and $W(1)-S_b$ of 2.238(3) and 2.237(3) Å are comparable with that observed in the Mo–W–S compound $[(OC)_4MoS_2W_2]^{2-}$ (2.230 Å) [5]. This leads to a mean value W(1)–S of 2.20(4) Å which is obviously longer than that observed in the free anion WS_4^{2-} (2.17 Å) [14] (see Table 7).

TABLE 5. Bond distances (Å) and bond angles (°) of the anion $[W(CO)_4(S_2CNEt_2)]^-$

W–S(1)	2.591(3)	C(2)–O(2)	1.15(2)
W–S(2)	2.636(5)	C(3)–O(3)	1.14(2)
W–C(1)	1.96(1)	C(4)–O(4)	1.18(2)
W–C(2)	1.92(2)	N(1)–C(10)	1.32(2)
W–C(3)	1.96(2)	N(1)–C(11)	1.47(3)
W–C(4)	2.04(2)	N(1)–C(13)	1.48(2)
S(1)–C(10)	1.71(2)	C(11)–C(12)	1.47(3)
S(2)–C(10)	1.74(2)	C(13)–C(14)	1.58(3)
C(1)–O(1)	1.15(2)		
S(1)–W–S(2)	66.9(2)	W–S(1)–C(10)	90.8(6)
S(1)–W–C(1)	164.1(5)	W–S(2)–C(10)	88.8(5)
S(1)–W–C(2)	104.0(6)	W–C(1)–O(1)	179.7(8)
S(1)–W–C(3)	89.1(5)	W–C(4)–O(4)	174(1)
S(1)–W–C(4)	96.9(5)	W–C(2)–O(2)	177(2)
S(2)–W–C(1)	97.3(5)	W–C(3)–O(3)	177(1)
S(2)–W–C(2)	170.1(6)	C(10)–N(1)–C(11)	123(1)
S(2)–W–C(3)	90.9(5)	C(10)–N(1)–C(13)	122(1)
S(2)–W–C(4)	89.1(5)	C(11)–N(1)–C(13)	116(1)
C(1)–W–C(2)	92.0(7)	S(1)–C(10)–S(2)	113.5(8)
C(1)–W–C(3)	88.9(6)	S(1)–C(10)–N(1)	125(1)
C(1)–W–C(4)	84.5(6)	S(2)–C(10)–N(1)	122(2)
C(2)–W–C(3)	93.2(8)	N(1)–C(11)–C(12)	112(1)
C(2)–W–C(4)	88.3(6)	N(1)–C(13)–C(14)	111(1)
C(3)–W–C(4)	173.3(7)		

Numbers in parentheses are e.s.d.s. in the least significant digits.

TABLE 6. Bond distances (Å) and bond angles (°) of the anion $[(CO)_4WS_2WS_2]^{2-}$

W(1)–W(2)	3.0103(7)	W(2)–C(1)	1.91(1)
W(1)–S(1)	2.238(3)	W(2)–C(2)	1.95(1)
W(1)–S(2)	2.237(3)	W(2)–C(3)	2.03(1)
W(1)–S(3)	2.161(3)	O(1)–C(1)	1.22(1)
W(2)–S(1)	2.531(3)	O(2)–C(2)	1.18(1)
W(2)–S(2)	2.539(3)	O(3)–C(3)	1.15(2)
S(1)–W(1)–S(2)	110.9(1)	S(2)–W(2)–C(3)	88.6(3)
S(1)–W(1)–S(3)	108.60(8)	C(1)–W(2)–C(2)	91.6(5)
S(2)–W(1)–S(3)	109.19(8)	C(1)–W(2)–C(3)	90.0(2)
S(3)–W(1)–S(3)	110.4(2)	C(2)–W(2)–C(3)	91.5(3)
S(1)–W(2)–S(2)	93.2(1)	C(3)–W(2)–C(3)	177.2(5)
S(1)–W(2)–C(1)	176.3(4)	W(1)–S(1)–W(2)	78.03(9)
S(1)–W(2)–C(2)	84.7(3)	W(1)–S(2)–W(2)	77.9(1)
S(1)–W(2)–C(3)	90.0(2)	W(2)–C(1)–O(1)	180(1)
S(2)–W(2)–C(1)	90.5(5)	W(2)–C(2)–O(2)	176(2)
S(2)–W(2)–C(2)	177.9(3)	W(2)–C(3)–O(3)	174.2(9)

Numbers in parentheses are e.s.d.s. in the least significant digits.

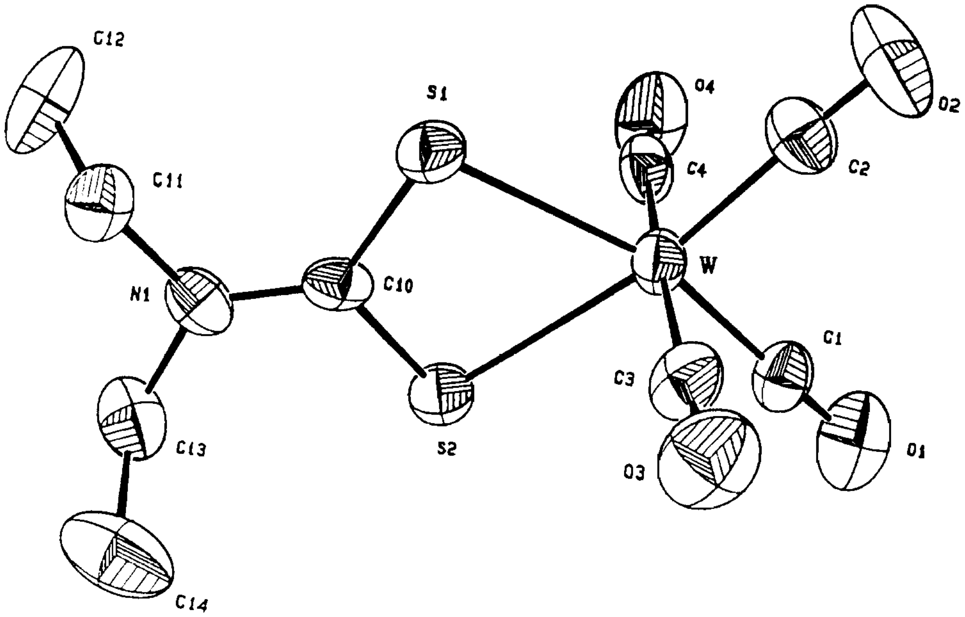

Fig. 1. Structure of the anion $[W(CO)_4(S_2CNEt_2)]^-$.

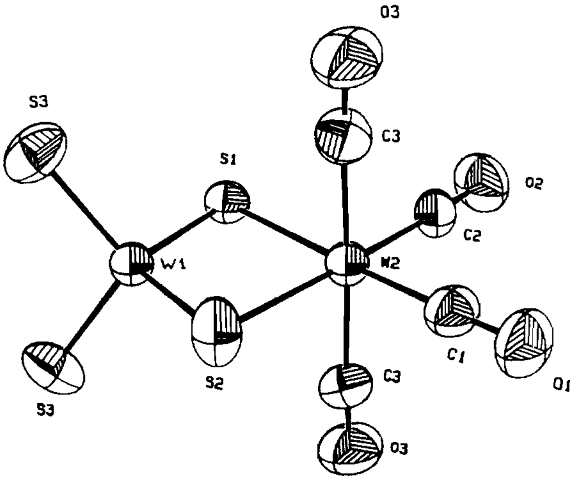

Fig. 2. Structure of the anion $[(OC)_4WS_2WS_2]^{2-}$.

On account of the fact that the two tungsten atoms in 2 possess two different W–S_b bond distances (2.535(6) and 2.238(1) Å) and are located at two different coordination environments, it is without doubt that the two W atoms are in different oxidation states and the W atom located at the center of the octahedron is probably in the low oxidation state, because of the necessity of coordination of carbonyls for stabilization and the longer tungsten–sulfur bond distance of 2.535(6) Å which is comparable with the one observed in W(0) complexes $[W_2(CO)_8(SPh)_2]^{2-}$ [11], $[W(CO)_4(S_2CNEt_2)]^-$. Considering the suggestion that Fe–M charge transfer is evident in the Fe–M–S complexes when the mean values of the Fe–ligand bond lengths and of the M–S bond lengths in the MS_4^{2-} ligands are taken into account [10], it can be found that, similarly, a $W(2) \rightarrow W(1)S_4$ charge transfer should exist in **2** because, as shown in Table 7, the W–S bond length in the WS_4^{2-} ligand of **2** is rather longer than that in the free WS_4^{2-} ion and the W–C bond distance is longer than that observed in the W(0) complex, $[W(CO)_4(S_2CNEt_2)]^-$. However, even if W–WS_4^{2-} electron delocalization exists, the two tungsten atoms in **2** are still in very different oxidation states, which will result in the redox that occurs on two different metal centers. As a matter o fact, **2** exhibits two sets of CV behavior (see below).

Cyclic voltammetry of 1 and 2

Cyclic voltammograms of **1** and **2** in MeCN at the glassy carbon electrode are depicted in Figs. 3 and 4, respectively. As shown in Fig. 3, the irreversible oxidation peaks at +0.15, +0.36 and +0.64 V versus SCE are very similar to those found in $[Mo(CO)_4(S_2CNEt_2)]^-$ (+0.14, +0.26 and +0.44 V versus SCE) [8], except that in the former the values of potential show a somewhat positive shift, and the absence of the peak at 0.004 V which was observed in $[Mo(CO)_4(S_2CNEt_2)]^-$ assigned to the redox derived from $2dtc \rightarrow (dtc)_2 + 2e^-$ [16]. These just mean the oxidation of **1** and the dissociation of $[S_2CNEt_2]^-$ from **1** are more difficult than that of $[Mo(CO)_4(S_2CNEt_2)]^-$, therefore it is not difficult to understand the fact that the reaction of **1** with WS_4^{2-} needs a higher reaction temperature.

The cyclic voltammogram of **2** in MeCN (Fig. 4) exhibits a pseudo-reversible redox couple at −2.11

TABLE 7. The selected average bond distances (Å) of several compounds with WS_4^{2-} and/or the $W(CO)_4$ moiety[a]

	W_2–C	W_2–S_b	W_1–S_b	W_1–S_t	W_1–S	Reference
$[W(CO)_4(S_2CNEt_2)]^-$	1.97(5)	2.61(3)				this work
$[(OC)_4WS_2WS_2]^{2-}$	1.98(6)	2.535(6)	2.238(1)	2.161(3)	2.20(4)	this work
$[(OC)_4MoS_2WS_2]^{2-}$			2.230(1)	2.154(2)	2.19(5)	5
$[S_5FeS_2WS_2]^{2-}$			2.25(1)	2.16(2)	2.20(7)	11
$[(PhS)_2FeS_2WS_2]^{2-}$			2.25(1)	2.157(3)	2.20(6)	13
$[S_2WS_2FeS_2WS_2]^{3-}$			2.239(5)	2.166(9)	2.20(5)	12
$[(DMF)_2Fe(S_2WS_2)_2]$			2.213(2)	2.164(4)	2.19(3)	15
WS_4^{2-}					2.17(1)	14

[a] W_1 is the W atom in the WS_4 moiety. W_2 is the W atom in the $W(CO)_4$ moiety. The standard deviations of the averages were taken as the deviation from the mean $s=[(\Sigma x^2-n\bar{x}^2)/(n-1)]^{1/2}$.

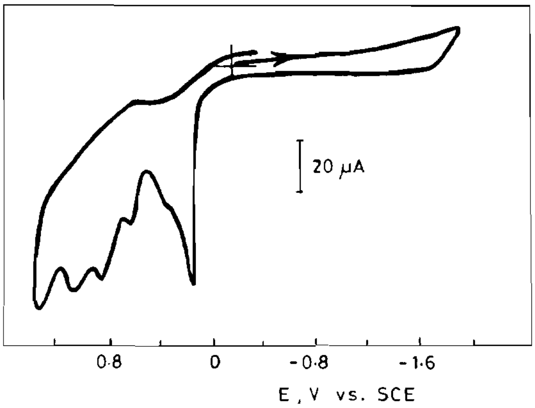

Fig. 3. Cyclic voltammogram of $[Et_4N][W(CO)_4(S_2CNEt_2)]$ in MeCN. Scan rate: 100 mV/s. Concentration of $[Et_4N][W(CO)_4(S_2CNEt_2)]$: 0.002 M.

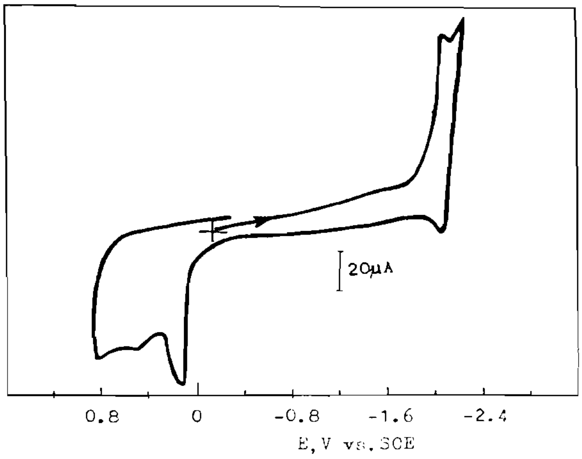

Fig. 4. Cyclic voltammogram of $[Et_4N]_2[(OC)_4WS_2WS_2]$ in MeCN. Scan rate: 100 mV/s. Concentration of $[Et_4N]_2[(OC)_4WS_2WS_2]$: 0.002 M.

V versus SCE and an irreversible oxidation peak at +0.12 V versus SCE. Referring to the electrochemical behaviors of low valence metal species such as $[W(CO)_4(S_2CNEt_2)]^-$, $[Mo(CO)_4(S_2CNEt_2)]^-$ [8] and $[Mo(CO)_5(SPh)]$ [17] which undergo irreversible oxidation at +0.14 to +0.17 V versus SCE, the irreversible oxidation peak at +0.12 V versus SCE is obviously due to the oxidation of the low-valence W-center in the $W(CO)_4$ moiety of **2**, the potential of the pseudo-reversible redox couple at −2.11 V versus SCE is comparable with the one observed in $[(OC)_4MoS_2WS_2]^{2-}$ (−2.33 [17]; −2.15 V versus SCE*). It is reasonable to assign this reversible redox couple to the redox which occurs on the higher W-center of the WS_4^{2-} moiety of **2**, according to the electrochemical data on the similar Fe–Mo–S species, [*o*-xyl-$S_2FeS_2MS_2$] (M = Mo, W) which contain the MS_4 moiety bound to an Fe thiolate and undergo reversible reduction at −1.6 (M = Mo) and −1.8 (M = W) V, events postulated on the bases of EPR spectroscopic evidence to involve formation of M(V) [17, 18]. It is worth noting that the value of −2.11 V versus SCE in **2** is more negative than the one in the free anion MS_4^{2-} (= Mo, 1.08 V versus SCE) [19]. This indicates the lowering of the electron density at the MS_4 center due to its ligating to the $M(CO)_4$ moiety (M = Mo, W), and is evidence for the existence of $W(0) \rightarrow WS_4$ electron delocalization.

Acknowledgements

Financial support by The Chinese National Science Foundation and The Chinese Academy of Sciences Foundation is gratefully acknowledged.

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*The data was obtained by measurement of sample, $[Et_4N][(OC)_4MoS_2WS_2]$ in identical conditions in this lab.

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