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Reactivity of Metal(0) Dithiocarbamato Carbonyl Complex $[M(CO)_4(S_2CNEt_2)]^-$ (M = Mo, W): a New Synthesis and Structure of a Mixed-metal Mo–W–S Complex $[Et_4N]_2[(OC)_4MoS_2WS_2]$

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Abstract

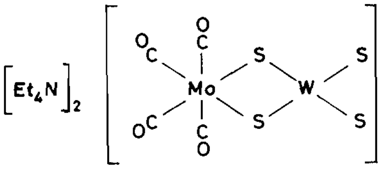
The reaction of molybdenum(0) dithiocarbamato carbonyl complex $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ with tetraethylammonium tetrathiotungstate $[Et_4N]_2[WS_4]$ in acetonitrile or methanol affords the dinuclear mixed-metal Mo–W–S complex, $[Et_4N]_2[(OC)_4MoS_2WS_2]$ (**1**). **1** was characterized by routine elemental analysis and spectroscopy and its structure was studied by X-ray crystallography. **1** crystallizes in the orthogonal, space group *Pbcm* with $a = 18.453(2)$, $b = 12.004(2)$, $c = 13.494(3)$ Å; $V = 2988.9$ Å^3; $Z = 4$; $D_c = 1.73$ g/cm^3; $R_1 = 0.032$ and $R_2 = 0.041$ for 1971 independent reflections ($I > 3\sigma(I)$). The structure of the anion of **1** is composed of an octahedron around the molybdenum atom and a tetrahedron with the tungsten atom in the center sharing an edge whcih is the line between the two bridged sulfur atoms. The Mo···W bond distance is 3.0330(8) Å and the bimetallic center MoS_2W is planar with the MoSW angles of 78.74(6)° and 78.42(7)°. The longer average bond distances of Mo–CO and W–S indicate the existence of a Mo $\rightarrow$ WS_4 electron delocalization in **1** which is similar to the charge transfer in the linear Fe–Mo–S cluster compounds. The new route to synthesize **1** is also discussed.

Introduction

The chemistry of molybdenum complexes containing an Mo–S bond has increasingly attracted the attention of chemists and bioinorganic chemists because of the existence of Mo–S bonding in a variety of molybdenum-containing enzymes, among them nitrogenase [1–3], and the appearance of hydrodesulfurization catalysts containing Mo and S atoms [4].

To introduce the molybdenum atom in a low oxidation state into cluster compounds containing an Mo–S bond and to build the mixed-metal clusters with mixed-valence, which will be interesting from a structural point of view and will possess unusual electronic properties and will exhibit available reactivities, is one of the aims of our recent research on molybdenum–sulfur complexes with molybdenum in the low oxidation state [5–9]. During our study on the reactivity of a new metal(0) dithiocarbamato carbonyl complex $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ synthesized by our research group recently [8] we found a new synthetic route for the mixed-metal Mo–W–S complex $[Et_4N]_2[(CO)_4MoS_2WS_2]$ (**1**) which had been reported without crystal structure determination by Rosenheim and McDonald [10].

Herein we report the new synthesis and X-ray crystal structure of **1** and discuss the charge transfer in **1** by comparison with some complexes containing $Mo(CO)_4$ or WS_4 structural units. The new synthetic route is also discussed.



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Experimental

Materials and Methods

Acetonitrile was distilled from CaH_2. Methanol and isopropanol were dried by distillation with magnesium methoxide. The complex $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ [8] and the tetraethylammonium tetrathiotungstate $[Et_4N]_2[WS_4]$ [11] were prepared by the literature methods. All synthetic reaction procedures, crystal growth and preparation of the sample for X-ray determination were carried out under nitrogen atmosphere using the Schlenk technique and degassed solvents. All reactants were also degassed before use.

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Instrumentation

Perkin-Elmer 577 Infrared Spectrometer; Enraf Nonius CAD-4 Diffractometer; Carlo Erba Strumentazion Elemental Analyzer-MOD 1106.

Synthesis of $[Et_4N]_2[(OC)_4MoS_2WS_2]$ (1)

(a) To a mixture of $[Et_4N]_2[WS_4]$ (0.572 g, 1 mmol) and $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ (0.486 g, 1 mmol) was added 50 ml of methanol and the reaction mixture then was stirred at 55–60 °C for 24 h resulting in a dark colored solution. After cooling to room temperature some dark brown microcrystals precipitated from the dark reaction solution. The resulting reaction mixture was cooled at 4 °C overnight in order to complete the precipitation. A total of 0.48 g of brown microcystalline product **1** was obtained by filtration, washed with methanol and dried *in vacuo*. Yield, 61.5%. *Anal.* Calc. for $C_{20}H_{40}MoO_4S_4W$: C, 30.76; H, 5.17; N, 3.58; S, 16.41, W, 23.59. Found: C, 29.82; H, 5.36; N, 4.02; S, 16.04 and W, 22.70%. Observed in the IR spectrum (KBr pellet) of the product **1**, four strong absorption bands (2004, 1870, 1855 and 1825 cm^{-1}) in the range of 1600–2100 cm^{-1} and four low-energy bands at 475(m), 465(m), 450(sh) and 420(w) cm^{-1}, which are characteristic of terminal and bridging M–S (M = Mo, W) vibrations in linear, polynuclear, sulfido-compounds, indicate that the product **1** contains $Mo(CO)_4$ and S_2WS_2 units. Taking the existence of the characteristic peaks of the cation Et_4N^+ in the IR spectrum and the elemental analysis data together, this product is well consistent with the formula **1**.

(b) The mixture of $[Et_4N]_2[WS_4]$ (0.572 g, 1 mmol) and $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ (0.486 g, 1 mmol) in 40 ml of acetonitrile was stirred at 55–60 °C for 24 h resulting in a dark red solution. After cooling to room temperature and filtration, the resulting filtrate was evaporated *in vacuo* to about 10 ml and 50 ml of isopropanol was added. A total of 0.35 g of microcrystalline product **1** in an analytical pure state was collected by cooling at 4 °C for several hours, filtering, washing with methanol and drying *in vacuo*. Yield, 45%.

Reaction of $[Et_4N]_2[WS_4]$ with $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ in MeOH (or MeCN) with Variation of Reaction Temperature and Reactant Ratio

Reaction 1. $[Et_4N]_2[WS_4]$ (0.576 g) was reacted with 0.486 g of $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ in 50 ml of MeOH at 35–45 °C for 24 h. A total of 0.43 g of **1** was obtained after cooling, filtering, washing with MeOH and drying *in vacuo*. Yield, 55%.

Reaction 2. A mixture of 1 mmol $[Et_4N]_2[WS_4]$ and 2 mmol of $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ in 80 ml of MeOH was stirred at 55–60 °C for 24 h and then cooled at 4 °C overnight. The resulting dark mixture was filtered and 0.70 g of a dark brown solid product (**2**) was collected after washing with methanol and drying *in vacuo*. *Anal.* Calc. for $C_{24}H_{40}N_2Mo_2O_8S_4W$: C, 29.15; H, 4.08; N, 2.83. Found: C, 28.41; H, 4.17; N, 2.90%. IR (KBr pellets): 2000(s), 1900(s), 1865(s), 1820(s), 450(w) and 420(w) cm^{-1}. Obviously, in contrast to the IR spectrum of **1** the characteristic absorption bands of the W–S_t vibration at 475 and 465 cm^{-1} observed in **1** are absent in the IR spectrum of **2**. Taking account of the elemental analysis data of **2** there is no doubt that **2** is the trinuclear Mo–W–S cluster, $[Et_4N]_2[(OC)_4MoS_2WS_2Mo(CO)_4]$.

Reaction 3. A total of 0.572 g (1 mmol) of $[Et_4N]_2[WS_4]$ was reacted with 0.972 g (2 mmol) of $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ in 40 ml of MeCN at 45–55 °C for 24 h resulting in a deep red solution with a small amount of white residue in it. After cooling to room temperature and filtering, the red filtrate was evaporated *in vacuo* to about 10 ml and 40 ml of isopropanol was added. A total of 0.28 g of **1** as red brown crystals was obtained by cooling at 4 °C overnight, filtering, washing with methanol and drying *in vacuo*. Yield, 36%. It seems that no trinuclear complex **2** was isolated in this way.

Reaction 4. $[Et_4N]_2[WS_4]$ (1 mmol) was reacted with 1 or 2 mmol of $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ in 40 ml of MeCN at 82 °C for 24 h resulting in a dark solution. After cooling to room temperature, evaporating *in vacuo* and adding isopropanol, a great deal of unknown dark brown solid was precipitated. Only a small amount of **1** was isolated from the filtrate by cooling at 4 °C overnight.

X-ray Determination of Crystal Structure

A single crystal of **1** with approximate dimensions of 0.20 X 0.20 X 0.40 mm was grown from the mixed-solvent of MeCN and isopropanol. **1** crystallizes in the orthogonal, space group *Pbcm*, with a = 18.453(2), b = 12.004(2), c = 13.494(3) Å; V = 2988.9 $Å^3$; Z = 4; D_c = 1.73 g/cm^3. From the systematic absences of: $h0l$ ($l = 2n$) $0kl$ ($k = 2n$) and from subsequent least-squares refinement, the space group was determined to be *Pbcm*.

A total of 2927 unique reflections was collected at room temperature on an Enraf-Nonius CAD-4 computer controlled Kappa Axis diffractometer with graphite monochromator Mo Kα radiation (λ = 0.71073 Å) in the range of $0 < 2\theta < 52°$ using the $\omega-2\theta$ scan technique. Lorentz, polarization and linear decay corrections were applied to the data. The linear absorption coefficient is 46.3 cm^{-1} for Mo Kα radiation and no absorption correction was made. Only 1971 independent reflections ($I > 3\sigma(I)$) were used in the structure analysis.

The structure was solved by direct methods. The Mo and W atoms were located first and the remaining atoms were located in succeeding differ-

TABLE 1. Positional and thermal of parameters of $[Et_4N]_2[(OC)_4MoS_2WS_2]$ (1)[a]

Atom	*x*	*y*	*z*	*B* (Å^2)
W	0.80561(2)	0.05118(3)	0.7500(0)	3.041(7)
Mo	0.68779(4)	−0.12499(6)	0.7500(0)	3.16(2)
S(1)	0.6870(1)	0.0863(2)	0.7500(0)	3.29(4)
S(2)	0.8260(1)	−0.1318(2)	0.7500(0)	5.12(6)
S(3)	0.8530(1)	0.1240(2)	0.8807(2)	5.70(4)
O(1)	0.6781(4)	−0.3846(6)	0.7500(0)	6.4(2)
O(2)	0.5204(3)	−0.0982(7)	0.7500(0)	5.8(2)
O(3)	0.6854(3)	−0.1237(5)	0.5151(4)	7.4(2)
C(1)	0.6816(4)	−0.2873(8)	0.7500(0)	4.2(2)
C(2)	0.5830(5)	−0.1114(8)	0.7500(0)	4.1(2)
C(3)	0.6879(3)	−0.1242(5)	0.5990(6)	4.7(2)
N(1)	0.5967(4)	0.2500(0)	0.0000(0)	3.5(1)
C(11)	0.5524(4)	0.2642(7)	0.0913(6)	6.1(2)
C(12)	0.4969(5)	0.3571(9)	0.0888(7)	8.7(3)
C(13)	0.6435(4)	0.1471(6)	0.0110(6)	5.7(2)
C(14)	0.6951(4)	0.1459(8)	0.0958(7)	7.3(2)
N(2)	0.0812(4)	0.5130(6)	0.2500(0)	3.6(2)
C(21′)	0.0871(7)	0.6183(9)	0.320(1)	4.4(3)
C(21)	0.0130(6)	0.514(1)	0.192(1)	4.2(3)
C(22)	0.0152(4)	0.6241(7)	0.1151(6)	7.0(2)
C(23)	0.1499(6)	0.513(1)	0.193(1)	5.1(3)
C(23′)	0.0745(8)	0.408(1)	0.178(1)	4.9(3)
C(24)	0.1450(5)	0.4043(7)	0.1110(7)	7.4(2)

[a] e.s.d.s given in parentheses.

ence Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined by full-matrix least-squares and the final cycle of refinement included 177 variable parameters and converged (largest parameter shift is 0.24 times its e.s.d.) with unweighted and weighted agreement factors of

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.032$$

and

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.041$$

where the weight *w* is defined as by the Killean and Lawrence method [12] with terms of 0.020 and 1.0. The e.s.d. of observation of unit weight is 1.42.

The final positional and thermal parameters with estimated standard deviations are listed in Table 1.

Results and Discussion

New Route to Synthesize $[Et_4N]_2[(OC)_4MoS_2WS_2]$ (1)

The compound $[Et_4N]_2[(OC)_4MoS_2WS_2]$ (**1**) was first reported in 1987 by Rosenhein and McDonald [10] although the crystal structure had not been determined. Its synthesis was from the reaction of $Mo(CO)_4(C_7H_8)$ with $[Et_4N]_2[WS_4]$ in MeOH. Recently we have found a new molybdenum(0) dithiocarbamato carbonyl complex $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ which is capable of providing a reactive fragment with the molybdenum atom in a low oxidation state by dissociation of dithiocarbamate ligand or substitution of carbonyls under certain reaction condition [8]. Using this complex instead of $Mo(CO)_4(C_7H_8)$ we developed a new route for the synthesis of **1** in good yield and in a convenient manner.

Reaction of one equiv. of $[Et_4N]_2[WS_4]$ with $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ in warm MeOH or MeCN afforded **1** according to eqn. (1).

$$\begin{gathered}[Et_4N]_2[WS_4] \\ + [Et_4N][Mo(CO)_4(S_2CNET_2)] \xrightarrow[55-60\ ^\circ C]{MeCN\ or\ MeOH} \\ [Et_4N]_2[(OC)_4MoS_2WS_2] + Et_4N^+ + [S_2CNEt_2]^- \qquad (1)\end{gathered}$$

This preparative reaction seems to be a simple one involving dissociation of the S_2CNEt_2 ligand and substitution by the bidentate ligand $S_2WS_2^{2-}$. As shown in Table 2, rise of the reaction temperature increased the yield of **1** but the yield decreased dramatically when the temperature reached 82 °C due to, perhaps, the decomposition of reactants or product. The solvent seems to influence the solubility of the starting materials and products and dissociation of the product. For MeOH, the solubilities of both the dinuclear product **1** and trinuclear product **2** are much less resulting in the easier isolation of the product from the preparative reaction. For MeCN, the solubilities of both **1** and **2** are much greater so that the isolation of the product needs a second solvent such as isopropanol to lower their solubilities. Noteworthily, the fact that when the 2:1

TABLE 2. The influence of reaction conditions on the formation and yield of product

Ratio of reactants $[Mo(CO)_4(S_2CNEt_2)]^-:WS_4^{2-}$	Temperature (°C)	Solvent	Product (%)
1:1	55–60	MeOH	**1** (61%)
1:1	55–60	MeCN	**1** (45%)
1:1	35–45	MeOH	**1** (55%)
2:1	45–55	MeCN	**1** (36%)
2:1	55–60	MeOH	**2** (70%)
2:1 or 1:1	82	MeCN	**1** (poor)

ratio of $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ to $[Et_4N]_2[WS_4]$ was used in the preparative reaction, the trinuclear compound 2 could be isolated in high yield if MeOH was used as solvent and the dinuclear compound 1 was obtained in a yield of 36% if the reaction solvent was MeCN, implies the existence of dissociation of the trinuclear compound 2 into 1 in MeCN following equilibrium (2).

$$[Et_4N]_2[(OC)_4MoS_2WS_2Mo(CO)_4] + Et_4N^+ + [S_2CNEt_2]^- \rightleftharpoons [Et_4N]_2[(OC)_4MoS_2WS_2] + [Mo(CO)_4(S_2CNEt_2)]^- + Et_4N^+ \qquad (2)$$

A similar equilibrium has been observed in DMF solution of $[Cl_2FeS_2MoS_2FeCl_2]^{2-}$ [13] and a greater solubility of 2 in MeCN–isopropanol. This is the reason why only the dinuclear complex 1 could be isolated without any contamination of 2.

Owing to the easier synthesis of the molybdenum(0) dithiocarbamato carbonyl complex $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$, the possibility to extend it to a W analog and the reactivity of $[M(CO)_4(S_2CNEt_2)]^-$ (M = Mo, W), the synthetic route by means of $[M(CO)_4(S_2CNEt_2)]^-$ (M = Mo, W) will be available for building a variety of mixed-metal and mixed-valence cluster compounds with Mo or W in a low oxidation state. As a matter of fact, this has led to our successful synthesis of a series of new Mo(W)–W(Mo)–S complexes the investigation results of which will be reported elsewhere.

The Structure of $[Et_4N]_2[(OC)_4MoS_2WS_2]$ and Mo → WS_4 Electron Delocalization

The bond distances and angles of the anion of 1 are given in Tables 3 and 4 respectively and the molecular structure of the anion of 1 is depicted in Fig. 1. 1 is composed of two discrete cations, Et_4N^+, and one dinuclear anion, $[(OC)_4MoS_2WS_2]^{2-}$. As shown in Fig. 1, in the anion of 1 the Mo atom is located at the center of an octahedron comprising four carbon atoms from the terminal carbonyls and two bridging sulfur atoms and the geometry around the W atom is a tetrahedron composed of two terminal sulfur atoms and two bridging S atoms. The whole anion of 1, $[(OC)_4MoS_2WS_2]^{2-}$, can be considered to be the structure which consists of the octahedron with the Mo atom and the tetrahedron containing the W atom sharing an edge (the line between the two bridging S atoms) and possesses a symmetric mirror with Mo, W, 2 bridging S and 2 C atoms (*trans* to the bridging S) on it and a pseudo-C_2 through the Mo and W atoms. The Mo···W bond distance is 3.0330(8) Å and the W–S_t bond distance of 2.154(2) Å is comparable with that in Fe–W–S complexes $[(S_5)FeS_2WS_2]^{2-}$ (2.157 Å) [14] and $[(PhS)_2FeS_2WS_2]^{2-}$ (2.157 Å) [15]. The two Mo–CO bond distances *trans* to the bridging sulfur atoms (1.95(1) and 1.94(8) Å) are shorter than the other two (2.038(8) Å) due to the *trans*-effect. The bimetallic unit MoS_2W with Mo–S_b bond distances of 2.537(3) and 2.553(2) Å, W–S_b bond lengths of 2.230(2) and 2.229(2) Å, MoSW angles of 78.74(6)° and 78.42(7)°, SWS angle of 110.65(8) and SMoS angle of 92.19(6)° is planar.

TABLE 3. Bond distances (Å) of $[(OC)_4MoS_2WS_2]^{2-}$

W–Mo	3.0330(8)	Mo–C(1)	1.95(1)
W–S(1)	2.230(2)	Mo–C(2)	1.941(8)
W–S(2)	2.229(2)	Mo–C(3)	2.038(8)
W–S(3)	2.154(2)	O(1)–C(1)	1.18(1)
Mo–S(1)	2.537(3)	O(2)–C(2)	1.166(9)
Mo–S(2)	2.553(2)	O(3)–C(3)	1.133(8)

TABLE 4. Bond angles (°) of $[(OC)_4MoS_2WS_2]^{2-}$

S(1)–W–S(2)	110.65(8)	S(2)–Mo–C(3)	90.0(2)
S(1)–W–S(3)	108.76(5)	C(1)–Mo–C(2)	91.5(3)
S(2)–W–S(3)	109.36(6)	C(1)–Mo–C(3)	90.3(2)
S(2)–W–S(3)	109.36(6)	C(1)–Mo–C(3)	90.3(2)
S(3)–W–S(3)	109.9(2)	C(2)–Mo–C(3)	90.0(2)
S(1)–Mo–S(2)	92.19(6)	C(2)–Mo–C(3)	90.0(2)
S(1)–Mo–C(1)	176.3(2)	C(3)–Mo–C(3)	179.4(3)
S(1)–Mo–C(2)	84.8(2)	W–S(1)–Mo	78.74(6)
S(1)–Mo–C(3)	89.7(2)	W–S(2)–Mo	78.42(7)
S(1)–Mo–C(3)	89.7(2)	Mo–C(1)–O(1)	180.1(6)
S(2)–Mo–C(1)	91.5(2)	Mo–C(2)–O(2)	177.0(7)
S(2)–Mo–C(2)	177.0(2)	Mo–C(3)–O(3)	177.6(6)
S(2)–Mo–C(3)	90.0(2)		

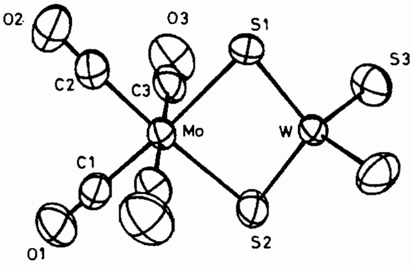

Fig. 1. Structure of the anion of 1, $[(OC)_4MoS_2WS_2]^{2-}$.

In the light of the structural data of 1 and some complexes containing the $Mo(CO)_4$ or S_2WS_2 moiety listed in Table 5, it is clear that when the S_2CNEt_2 ligand of $[Mo(CO)_4(S_2CNEt_2)]^-$ is substituted by the bidentate 'ligand' S_2WS_2 forming the complex 1, the average W–S bond length of 2.192 Å in 1 is longer than that in the $[WS_4]^{2-}$ anion (2.17 Å) [17] and also the mean value of Mo–CO (1.992 Å) in 1 is somewhat longer than that in the anion $[Mo(CO)_4(S_2CNEt_2)]^-$ (1.962 Å) [8]. By comparing the Mo(O) complex $[Mo_2(CO)_8(SCH_2CO_2Et)_2]^{2-}$ [6], and the Mo(I) compound, $[Mo_2(CO)_8(SCH_2CO_2Et)_2]$ [16], it is clearly seen that the Mo(O)–CO and

TABLE 5. Selected structural data of 1 and some complexes containing the $Mo(CO)_4$ and S_2WS_2 moiety

Complexes	$\overline{\text{Mo–CO}}$ (Å)	$\overline{\text{Mo–S}_\text{b}}$ (Å)	$\overline{\text{W–S}_\text{b}}$ (Å)	$\overline{\text{W–S}_\text{t}}$ (Å)	$\overline{\text{W–S}}$ (Å)	Reference
$[Mo(CO)_4(S_2CNEt_2)]^-$	1.965					8
$[Mo_2(CO)_8(SCH_2CO_2Et)_2]^{2-}$	1.985					6
$[Mo_2(CO)_8(SCH_2CO_2Et)_2]$	2.019					16
$[(OC)_4MoS_2WS_2]^{2-}$	1.992	2.545	2.230	2.154	2.192	this work
$[(S_5)FeS_2WS_2]^{2-}$			2.254	2.157	2.206	14
$[(PhS)_2FeS_2WS_2]^{2-}$			2.246	2.157	2.205	15
$[(DMF)_2Fe(S_2WS_2)_2]^{2-}$			2.213	2.164	2.189	21
$[Co(S_2WS_2)_2]^{2-}$			2.219	2.139	2.179	18
$[Zn(S_2WS_2)_2]^{2-}$			2.233	2.156	2.195	20
$[Ni(S_2WS_2)_2]^{2-}$			2.232	2.151	2.192	19
$[Hg(S_2WS_2)_2]^{2-}$			2.246	2.173	2.209	19
$[WS_4]^{2-}$					2.17	17

$\overline{\text{Mo(I)–CO}}$ average bond lengths in the complexes containing the $Mo(CO)_4$ moiety are 1.985 and 2.019 Å, repsectively and the $\overline{\text{Mo–CO}}$ value of 1.992 Å in 1 lies between the values of $\overline{\text{Mo(O)–CO}}$ and $\overline{\text{Mo(I)–CO}}$. This obviously indicates that the oxidation state of Mo atom in 1 should be situated between Mo(O) and Mo(I). The fact that the strong absorption peaks of ν(MoC–O) (2004, 1870, 1855 and 1827 cm^{-1}) observed in the IR spectrum of 1 are at higher wavenumbers than those observed in Mo(0) complexes, $[Mo(Co)_4[S_2CNEt_2)]^-$ [8] and $[Mo_2(CO)_8(SR)_2]^{2-}$ (R = CH_2CO_2Et [6], Ph [5, 7, 22], also suggests that the electron density on the Mo atom in 1 is lower than that on the Mo(0) atom. Because the electron density on the Mo atom is lower, the back-donation of electron to π^* of CO is less, as a result ν(MoC–O) shifts to a higher wavenumber.

Looking at the structural parameters of $M–WS_4$ (M = Fe, Co, Zn, Ni and Hg) complexes shown in Table 5, it is obvious that the dimension of the WS_4 moiety in 1 is very similar to that in those $M–WS_4$ complexes. In terms of the existence of Fe → W(Mo) charge transfer in the $Fe–W(Mo)S_4$ complexes which have been investigated and established by Mössbauer spectra, electronic spectra [23], IR spectra [24], resonance Raman spectroscopy [25] and theoretical study [19, 26], and taking the case of 1 discussed above into account, it is reasonable to come to the conclusion that a Mo → WS_4 electron delocalization exists in 1. This is well consistent with the result from the electrochemical study by Rosenhein and McDonald [10].

Acknowledgements

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