Synthesis, Structure and Electrochemistry of $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]_2[Mo_6O_{19}] \cdot 2CH_3COCH_3$

Fang-Hui Wu[a,b], Yang-Li Liu[b], Taike Duan[b], Lude Lu[a], Qian-Feng Zhang[b], and Wa-Hung Leung[c]

[a] Material Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing 210094, P. R. China
[b] Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology, Ma'anshan, Anhui 243002, P. R. China
[c] Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, P. R. China

Reprint requests to Dr. Qian-Feng Zhang. Fax: +86-555-2312041. E-mail: zhangqf@ahut.edu.cn

Z. Naturforsch. **2009**, *64b,* 800 – 804; received February 11, 2009

Reaction of $MoO_2(S_2CNMe_2)_2$ with $RuCl_3 \cdot xH_2O$ in acetone at reflux afforded $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]_2[Mo_6O_{19}]\cdot 2CH_3COCH_3$ ($\mathbf{1}\cdot 2CH_3COCH_3$) which was characterized by single-crystal X-ray diffraction to show a dinuclear ruthenium-dithiocarbamate species as cation and hexamolybdate as counter anion. The $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]^+$ cation may be considered as a combination of $[Ru(S_2CNMe_2)_3]$ with a *cis*-$[Ru(S_2CNMe_2)_2]^+$ species, and the Lindqvist anion $[Mo_6O_{19}]^{2-}$ is located on an inversion center between two cations. Spectroscopic properties along with the electrochemistry of compound $\mathbf{1}\cdot 2CH_3COCH_3$ are reported.

Key words: Ruthenium, Dithiocarbamate, Hexamolybdate, Synthesis, Crystal Structure, Electrochemistry

Introduction

Transition metal complexes of *N*,*N*-dialkyldithiocarbamates (R_2NCS_2) are of interest because of their resemblance to the active centers of metal-sulfur proteins [1]. It is very remarkable to note that Matsumoto and co-workers demonstrated electron-rich ruthenium dithocarbamate complexes to be potentially useful for multielectron catalysis [2]. Although dithocarbamate complexes of ruthenium are well-known, the most widely studied are the coordinatively saturated binary Ru(II) and Ru(III) complexes [3]. The typical tris-chelate complexes $Ru(S_2CNR_2)_3$ (R = alkyl) are very stable both in solution and in the solid state [4, 5], however, several interesting reactions may result in the formation of new complexes with new structural modes. For example, the reaction of $Ru(S_2CNEt_2)_3$ with BF_3 gas under aerobic conditions gave a mixed-valence Ru(II)-Ru(III) complex $[Ru_2(S_2CNEt_2)_5][BF_4]$ [6], and treatment of $Ru(S_2CNEt_2)_2(DMSO)_2$ (DMSO = dimethyl sulfoxide) with I_2 gave the linear Ru(II)-Ru(III)-Ru(III) trimer $[Ru_3(S_2CNEt_2)_6(DMSO)_2](I_3)_2$ [7].

The current interest in polymolybdates arises from their compositional range and structural versatility, as well as important optical, magnetic, catalytic and medicinal properties [8, 9]. Many reactions in solution and in the solid state have shown that the formation of a particular polymolybdate depends on the nature of the cation and the reaction conditions. Hexamolybdates are an important class of polymolybdates because of the high symmetry of the anion and the concomitant capability to form interesting derivatives [10]. Examples of hexamolybdates crystallizing with complex cations as counterions are $[M_2(MeCN)_{10}][Mo_6O_{19}]_2$ (M = Re, Rh, Mo, W) [11], $[FeCl(DMF)_5][Mo_6O_{19}]$ [12], $[(18\text{-crown-6})K]_2[Mo_6O_{19}]\cdot H_2O$ [13], $[Mo_2(S_2CNEt_2)_4]_2[Mo_6O_{19}]$ [14], $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\eta\text{-}Ph_2PCH_2PPh_2)]_2[Mo_6O_{19}]\cdot 4THF$ [15], $[(PhC_5Me_5)Cl(MeCN)_2]_2[Mo_6O_{19}]$ [16], $[Cu(H_2O)_4(\text{dibenzo-24-crown-8})][Mo_6O_{19}]$ [17], and $[Au_{11}(PPh_3)_8Cl_2]_2[W_6O_{19}]$ [18]. The $[Mo_6O_{19}]^{2-}$ anions in these complexes are acquired by anion exchange, while in some other cases they are produced by oxidation reactions of the corresponding low-valent molybdenum reactants, or by transformations of hexavalent molybdenum compounds. $[Ag(PPh_3)_4]_2[Mo_6O_{19}]\cdot 3CH_2Cl_2$ was obtained from the reaction of $Ag(PPh_3)_2NO_3$ and $K_4Mo(CN)_8$ in H_2O/CH_2Cl_2 in which oxidation of

0932–0776 / 09 / 0700–0800 \$ 06.00

Mo(IV) to Mo(VI) occurred due to the hydrolysis of $[Mo(CN)_8]^{4-}$ [19]. $[MoS_4Cu_4(\gamma\text{-Mepy})_4][Mo_6O_{19}]$ was synthesized from the reaction of $[MoS_4]^{2-}$ and copper(I) in γ-methylpyridine in which thiomolybdate(VI) hydrolyzed to hexamolybdate(VI) in an inert solvent [20]. $[MoNAr(S_2CNEt_2)_3]_2[Mo_6O_{19}]$ was isolated from the reaction of $MoO(Cl_2)(S_2CNEt_2)_2$ and $ArNH_2$ in the presence of triethylamine as a base [21]. A family of molybdates of composition $[Mo_2O_5L_6][Mo_6O_{19}]$ (L = H_2O, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, dibutyl sulfoxide, tributylphosphane oxide, triphenylphosphane oxide, hexamethylphosphoramide) were formed in the reactions of $MoO_2(acac)_2$ (acac = acetyacetonate) with ligands L under mild conditions [22]. The reactions involved the transformation of hexavalent molybdenum atoms only in certain compositions. As a part of our interest in ruthenium-sulfur chemistry, we devoted our efforts to develop the reactions of rutheniumdithiocarbamate-based complexes [23]. We report here the reaction of $MoO_2(S_2CNMe_2)_2$ and $RuCl_3\cdot xH_2O$ in wet acetone solution, which resulted in the formation of a new compound $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]_2$-$[Mo_6O_{19}]\cdot 2CH_3COCH_3$ (**1**·$2CH_3COCH_3$) with a dinuclear ruthenium dithiocarbamate species as cation and hexamolybdate as counter anion.

Experimental Section

General

All solvents were commercial products of high purity and used as received. $MoO_2(S_2CNMe_2)_2$ was prepared according to a procedure described in the literature [24]. $RuCl_3\cdot xH_2O$ was purchased from Alfa Ltd. The infrared spectrum was recorded on a Digilab FTS-40 spectrophotometer with use of pressed KBr pellets. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer. The magnetic moment of the solid sample was measured by a Sherwood magnetic susceptibility balance at r. t. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) model 273A potentiostat. The working and reference electrodes were glassy carbon and $Ag/AgNO_3$ (0.1 M in acetonitrile), respectively. Potentials were reported with reference to the ferrocenium-ferrocene ($Cp_2Fe^{+/0}$) couple.

*Synthesis of $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]_2[Mo_6O_{19}]\cdot 2CH_3COCH_3$ (**1**·$2CH_3COCH_3$)*

A mixture of $[MoO_2(S_2CNMe_2)_2]$ (74 mg, 0.20 mmol) and $RuCl_3\cdot xH_2O$ (40 mg, 0.15 mmol) was dissolved in acetone (25 mL) and the mixture stirred overnight at r. t. A color change from dark green to red was observed. Addition of 10 mL Et_2O resulted in a little grey-yellow precipitate. A clear red solution was obtained by filtration. Red block crystals of **1**·$2CH_3COCH_3$ were directly grown by slow evaporation from an acetone/Et_2O solvent mixture within a week. Yield: 57 mg, 41 %. – FT-IR (KBr, cm^{-1}): ν = 1714 (vs), 1662 (s), 1587 (vs), 1514 (s), 1461 (m), 1436 (m), 1383 (m), 1203 (m), 980 (s), 952 (m), 921 (vs), 902 (s), 849 (m), 806 (s), 775 (w), 745 (m), 658 (s), 487 (m). – Magnetic moment μ_{eff} = 1.89 μ_B at 296 K. – Anal. for $C_{36}H_{72}N_{10}O_{21}S_{20}Mo_6Ru_4\cdot 2(C_3H_6O)$: calcd. C 16.6, H 2.29, N 5.38; found C 16.2, H 2.23, N 5.33.

Table 1. Crystal data, data collection parameters and details of the structure refinement.

Complex	$[Ru_2(S_2CNEt_2)_3(\mu_3\text{-}S_2CNEt_2)_2]_2$ $[Mo_6O_{19}]\cdot 2CH_3COCH_3$
Empirical formula	$C_{36}H_{73}N_{10}O_{21}S_{20}Mo_6Ru_4$
Formula weight	2602.16
Color, habit	red, block
Crystal size, mm^3	$0.16\times 0.12\times 0.06$
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	14.9040(2)
b, Å	10.1775(1)
c, Å	26.8518(4)
β, deg	94.129(1)
Volume, Å^3	4062.46(9)
Z	2
Density (calcd.), g cm^{-3}	2.1
Absorption coefficient, mm^{-1}	2.193
Temperature, K	296(2)
F(000), e	2548
Radiation; wavelength, Å	MoK_α; 0.71073
Reflections collected	39266
Independence reflections	9313 (R_{int} = 8.64 %)
Reflections with $[I\geq 2\sigma(I)]$	5268
Parameters refined	451
Final $R1/wR2$ (all data)[a]	0.068/0.091
Goodness of fit (GoF)[b]	0.96
Final diff. peaks (max/min), e Å^{-3}	+0.54/−0.61

[a] $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2=[\Sigma w(|F_o{}^2|-|F_c{}^2|)^2/\Sigma w|F_o{}^2|^2]^{1/2}$, $w=[\sigma^2(F_o{}^2)+0.0306P^2+0.0000P]$, where $P=(F_o{}^2+2F_c{}^2)/3$; [b] $\text{GoF}=[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$.

Crystal structure determination

A single crystal of **1**·$2CH_3COCH_3$ was mounted on a glass fiber. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK_α radiation at 296 K using an ω scan mode. The collected frames were processed with the software SAINT [25]. The data were corrected for absorption using the program SADABS [26]. The structure was solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [27]. All non-hydrogen atoms were refined

Table 2. Selected bond lengths (Å) and angles (deg) for $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]_2[Mo_6O_{19}]\cdot 2Me_2CO$.

Ru(1)–S(1)	2.4057(15)	Ru(1)–S(2)	2.3975(17)
Ru(1)–S(3)	2.4131(16)	Ru(1)–S(4)	2.4044(16)
Ru(1)–S(5)	2.3320(15)	Ru(1)–S(10)	2.3148(17)
Ru(2)–S(5)	2.3057(16)	Ru(2)–S(6)	2.4131(16)
Ru(2)–S(7)	2.4063(15)	Ru(2)–S(8)	2.4219(15)
Ru(2)–S(9)	2.4060(16)	Ru(2)–S(10)	2.2963(15)
Ru(1)–Ru(2)	2.7930(6)	Mo(1)–O(2)	1.678(4)
Mo(1)–O(8)	1.898(4)	Mo(1)–O(4)	1.926(4)
Mo(1)–O(3)	1.932(4)	Mo(1)–O(1)	1.935(4)
Mo(1)–O(9)	2.3087(5)	Mo(2)–O(6)	1.677(4)
Mo(2)–O(10)	1.886(4)	Mo(2)–O(1)$^{\#1}$	1.928(4)
Mo(2)–O(4)	1.928(4)	Mo(2)–O(5)	1.953(4)
Mo(2)–O(9)	2.3262(5)	Mo(3)–O(7)	1.672(4)
Mo(3)–O(5)$^{\#1}$	1.887(4)	Mo(3)–O(3)$^{\#1}$	1.911(4)
Mo(3)–O(8)	1.955(4)	Mo(3)–O(10)	1.959(4)
Mo(3)–O(9)	2.3207(6)		
S(10)–Ru(1)–S(5)	104.78(5)	S(10)–Ru(1)–S(2)	163.80(6)
S(5)–Ru(1)–S(2)	88.70(6)	S(10)–Ru(1)–S(4)	90.97(6)
S(5)–Ru(1)–S(4)	101.41(6)	S(2)–Ru(1)–S(4)	95.18(6)
S(10)–Ru(1)–S(1)	98.74(6)	S(5)–Ru(1)–S(1)	87.34(5)
S(2)–Ru(1)–S(1)	72.52(5)	S(4)–Ru(1)–S(1)	164.90(6)
S(10)–Ru(1)–S(3)	86.21(6)	S(5)–Ru(1)–S(3)	167.52(6)
S(2)–Ru(1)–S(3)	81.48(6)	S(4)–Ru(1)–S(3)	72.05(6)
S(1)–Ru(1)–S(3)	96.94(6)	S(10)–Ru(2)–S(5)	106.24(6)
S(10)–Ru(2)–S(9)	74.24(5)	S(5)–Ru(2)–S(9)	101.43(6)
S(10)–Ru(2)–S(7)	157.99(6)	S(5)–Ru(2)–S(7)	93.60(5)
S(9)–Ru(2)–S(7)	92.84(5)	S(10)–Ru(2)–S(6)	107.36(6)
S(5)–Ru(2)–S(6)	74.50(5)	S(9)–Ru(2)–S(6)	175.88(6)
S(7)–Ru(2)–S(6)	86.78(6)	S(10)–Ru(2)–S(8)	90.11(5)
S(5)–Ru(2)–S(8)	161.93(5)	S(9)–Ru(2)–S(8)	90.23(5)
S(7)–Ru(2)–S(8)	71.85(5)	S(6)–Ru(2)–S(8)	93.56(5)
Ru(1)–S(5)–Ru(2)	74.06(5)	Ru(1)–S(10)–Ru(2)	74.56(5)

Symmetry code: $^{\#1}$ $-x$, $-y+2$, $-z+1$.

anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp^3}–H = 0.96 Å) and included in the structure factor calculations with assigned isotropic displacement parameters but were not refined. Crystal data, data collection parameters and details of the structure refinement are given in Table 1.

CCDC 719657 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.

Results and Discussion

When the mixture of $[MoO_2(S_2CNMe_2)_2]$ with an equivalent of $RuCl_3 \cdot xH_2O$ was refluxed in acetone solution, a new compound $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]_2[Mo_6O_{19}]\cdot 2CH_3COCH_3$ (**1**·$2CH_3COCH_3$) was formed and isolated in 41 % yield. Owing to the periodic relationship between ruthenium and molybdenum, ruthenium(III) obviously has a higher affinity to sulfur atoms of the dithocarbamate ligand than molybdenum(VI). The Me_2NCS_2 ligands are totally dissociated from $[MoO_2(S_2CNMe_2)_2]$ and bound to the ruthenium atom of the starting $RuCl_3 \cdot xH_2O$, along with the formation of $[Mo_6O_{19}]^{2-}$ anions in wet acetone. The strong peak at 1714 cm^{-1} for ν(C=O) in the IR spectrum indicated the presence of co-crystallized CH_3COCH_3 solvent molecules in compound **1**·$2CH_3COCH_3$. The bands near 1500 and 1000 cm^{-1} are very characteristic for the C=N and C–S stretching vibrations of the Me_2NCS_2 ligand [5]. IR data (peaks at 980, 921, 487 cm^{-1}) for **1**·$2CH_3COCH_3$ in the ν(Mo–O) region reveal the expected anion-dependent shifts of these vibrational modes as compared to the $[Bu^n{}_4N]_2[Mo_6O_{19}]$ salt [28]. Magnetic susceptibility measurement of the solid sample at r. t. indicated an effective magnetic moment $\mu_{\text{eff}} = 1.89\ \mu_B$, which might be explained in terms of a partial quenching of the magnetic moment of the $Ru(S_2CNMe_2)_3$ monomer (typical as $\mu_{\text{eff}} = 1.80\ \mu_B$) by spin-spin or similar interaction. This value may be indicative of Ru(III) in solid **1**·$2CH_3COCH_3$.

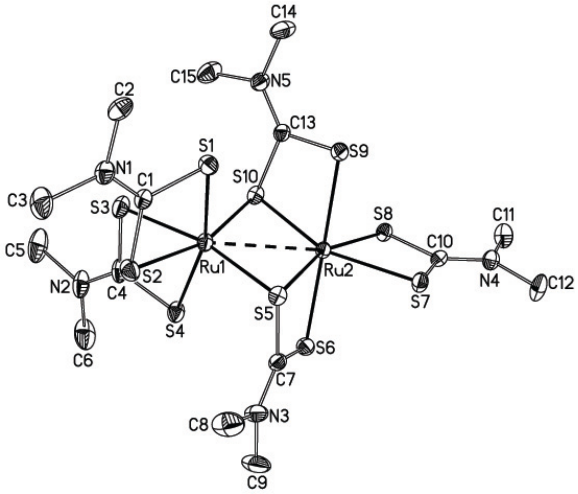

Fig. 1. Perspective view of the $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]^+$ cation in **1** with displacement ellipsoids drawn at the 40 % probability level.

The structure of compound **1**·$2CH_3COCH_3$ was confirmed by an X-ray diffraction study. Fig. 1 shows a perspective view of the cation $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]^+$; selected bond lengths and angles are given in Table 2. The asymmetric unit consists of two $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]^+$ cations, one $[Mo_6O_{19}]^{2-}$ anion, and two acetone molecules. The $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]^+$ cation may be considered as a combination of $[Ru(S_2CNMe_2)_3]$ with

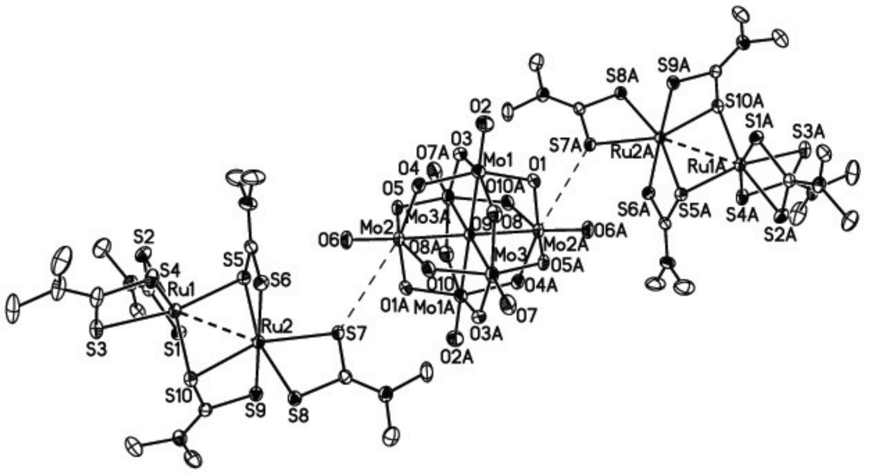

Fig. 2. ORTEP drawing of a $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]_2[Mo_6O_{19}]$ unit, showing weak intermolecular contacts between the cations and the anion.

a *cis*-$[Ru(S_2CNMe_2)_2]^+$ species, the $[Ru(S_2CNMe_2)_3]$ moiety acting as a ligand to the $[Ru(S_2CNMe_2)_2]^+$ unit by donotion of the *p*-*π* electrons from each of a pair of bridging sulfur atoms mutually *cis* from different ligands of the two compounds. Although a similar compound $[Ru_2(S_2CNMe_2)_5]_2[Ru_2Cl_6]$ with the same core structure of the cation has been reported [29], the current arrangement $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]_2$-$[Mo_6O_{19}]$ is the first example of a dinuclear ruthenium-dithiocarbamate species as cations and hexamolybdate as counter anion. The bonding mode of the dithiocarbamates in the $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]^+$ core of **1**·$2CH_3COCH_3$ is reminiscent of that of the reported monocation $[Ru_2(S_2CNMe_2)_5]^+$ in $[Ru_2(S_2CNMe_2)_5]_2[Ru_2Cl_6]$ [29]. The Ru(1)–Ru(2) distance (2.7930(6) Å) is slightly longer than those in $[Ru_2(S_2CNMe_2)_5]_2[Ru_2Cl_6]$ (2.788(4) Å) [29] and $[Ru_2(S_2CNEt_2)_5][BF_4]$ (2.743(3) Å) [6], and slightly shorter than that in $[Ru_3(S_2CNEt_2)_6(DMSO)_2](I_3)_2$ (2.826(2) Å) [7]. Compared to 2.650 Å for the Ru–Ru distance found in elemental ruthenium, the intermetallic distance in **1**·$2CH_3COCH_3$ is indicative of a metal–metal bond.

Three types of Ru–S bonds can be identified in the structure of **1**·$2CH_3COCH_3$. The average Ru–S bond lengths are 2.408(2) Å for terminal chelated ligands (S1, S2, S3, S4, S7 and S8), 2.410(2) Å for non-bridging sulfur atoms of mono-bridging ligands (S6 and S9), and 2.312(2) Å for the bridging ligands (S5 and S10), which are compatible with the corresponding Ru–S bond lengths in $[Ru_2(S_2CNMe_2)_5]_2$-$[Ru_2Cl_6]$ [29], $[Ru_2(S_2CNEt_2)_5][BF_4]$ [6] and $[Ru_3(S_2CNEt_2)_6(DMSO)_2](I_3)_2$ [7]. The four-membered ring formed by Ru(1), S(5), Ru(2) and S(10) is nearly planar with an average deviation of 0.045 Å from the least-squares plane. The average Ru–S–Ru angle in this ring of 74.36(5)° is to be compared with that in $[Ru_2(S_2CNMe_2)_5]_2[Ru_2Cl_6]$ (74.05(6)°) [29] and in $[Ru_2(S_2CNEt_2)_5][BF_4]$ (72.9(3)°) [6].

The hexamolybdate anion in **1**·$2CH_3COCH_3$ displays the well-known Lindqvist structure. The anion $[Mo_6O_{19}]^{2-}$ has its expected structure as well as normal distances and angles, which will not be discussed further. The unit cell contains one formula unit of $[Ru_2(S_2CNMe_2)_3(\mu_3\text{-}S_2CNMe_2)_2]_2[Mo_6O_{19}]$. The Lindqvist anion $[Mo_6O_{19}]^{2-}$ (O_h symmetry) is located on an inversion center between two cations, and its structure is shown in Fig. 2. Similar cases have been found in $[MoNAr(S_2CNEt_2)_3]_2[Mo_6O_{19}]$ [21] and $[Au_{11}(PPh_3)_8Cl_2]_2[W_6O_{19}]$ [18]. The separation between the molybdenum atom and one of the sulfur atoms of a chelating Me_2NCS_2 ligand is 3.888(2) Å, suggestive of weak intermolecular contacts between the dinuclear ruthenium dithiocarbamate cations and the hexamolybdate anions.

The cyclic voltammogram of **1**·$2CH_3COCH_3$ displays two reversible couples at 0.06 V and −0.79 V, tentatively assigned as the Ru(II,III)/Ru(III,III) and Ru(III,II) couples, respectively, along with an irreversible wave at −1.09 V. The oxidation of **1**·$2CH_3COCH_3$ occurs at 0.71 V *vs.* $Cp_2Fe^{+/0}$ and is an extremely accessible, quasi-reversible transition, which is assigned as the metal-centered Ru(III,III)/Ru(IV,IV) couple because the hexamolybdate anion and the free dithiocarbamate ligand are redox inactive at this potential. This suggests that the binuclear ruthenium species in **1**·$2CH_3COCH_3$ might be oxidized into a high-valent complex [7]. Further investigation on the isolation of high-valent ruthenium complexes in the electrochemically generated state is underway.

Acknowledgements

This project was supported by the Natural Science Foundation of China (20771003) and the Program for New Century Excellent Talents in University of China (NCET-06-0556). Dr. Q.-F. Zhang thanks the Natural Science Foundation of the Education Bureau of Anhui Province (2006kj035a) for the assistance.

---

[1] R. P. Burns, F. P. McCullough, C. A. McAuliffe, *Adv. Inorg. Nucl. Chem.* **1980**, *23*, 211.

[2] M. Kawano, H. Uemura, T. Watanabe, K. Matsumoto, *J. Am. Chem. Soc.* **1993**, *115*, 2068.

[3] G. Hogarth, *Prog. Inorg. Chem.* **2005**, *53*, 71.

[4] L. H. Pignolet, *Inorg. Chem.* **1974**, *13*, 2051.

[5] R. Eisenberg, *Prog. Inorg. Chem.* **1970**, *12*, 295.

[6] B. M. Marrson, J. R. Heiman, L. H. Pignolet, *Inorg. Chem.* **1976**, *15*, 564.

[7] W. H. Leung, J. L. C. Chim, H. Hou, T. S. M. Hun, I. D. Williams, W. T. Wong, *Inorg. Chem.* **1997**, *36*, 4432.

[8] M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34.

[9] D. L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105.

[10] Y. Wei, B. Xu, C. L. Barnes, Z. Peng, *J. Am. Chem. Soc.* **2001**, *123*, 4083.

[11] S. L. Bartley, S. N. Bernstein, K. R. Dunbar, *Inorg. Chim. Acta* **1993**, *213*, 213.

[12] S. Lu, J. Huang, Z. Huang, *Huaxue Xuebao (Chin.)* **1992**, *30*, 348.

[13] O. Nagano, Y. Sasaki, *Acta Crystallogr.* **1979**, *B35*, 2387.

[14] K. S. Jasin, C. Chieh, T. C. W. Mak, *J. Crystallogr. Spectrosc. Res.* **1985**, *15*, 403.

[15] V. Riera, M. A. Ruiz, F. Villatane, Y. Jeannin, C. Bois, *J. Organomet. Chem.* **1988**, *345*, C4.

[16] C. Zhang, Y. Ozawa, Y. Hayashi, K. Isobe, *J. Organomet. Chem.* **1989**, *373*, C21.

[17] V. Shivaiah, S. K. Das, *Inorg. Chem.* **2005**, *44*, 7313.

[18] M. Schulz-Dobrick, M. Jansen, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2326.

[19] D. L. Long, X. Q. Xin, X. M. Chen, B. S. Kang, *Polyhedron* **1997**, *16*, 1259.

[20] M. T. Pope, J. P. Lang, X. Q. Xin, K. B. Yu, *Chin. J. Chem.* **1995**, *13*, 40.

[21] M. Minelli, M. L. Hoang, M. Kraus, G. Kucera, J. Loertscher, M. Reynolds, N. Timm, M. Y. Chiang, D. Powell, *Inorg. Chem.* **2002**, *41*, 5954.

[22] M. R. Pedrosa, R. Aguado, V. Díez, J. Escribano, R. Sanz, F. J. Arnáiz, *Eur. J. Inorg. Chem.* **2007**, 3952.

[23] W. M. Cheung, Q. F. Zhang, I. D. Williams, W. H. Leung, *Inorg. Chim. Acta* **2006**, *359*, 782.

[24] B. W. Moore, M. L. Larson, *Inorg. Chem.* **1967**, *6*, 998.

[25] SMART and SAINT+ for Windows NT (version 6.02a), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **1998**.

[26] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **1996**.

[27] G. M. Sheldrick, SHELXTL, Software Reference Manual (version 5.1), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **1997**; see also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

[28] N. H. Hur, W. G. Klemperer, R. C. Wang, *Inorg. Chem.* **1990**, *27*, 77.

[29] C. L. Raston, A. H. White, *J. Chem. Soc., Dalton Trans.* **1975**, 2410.