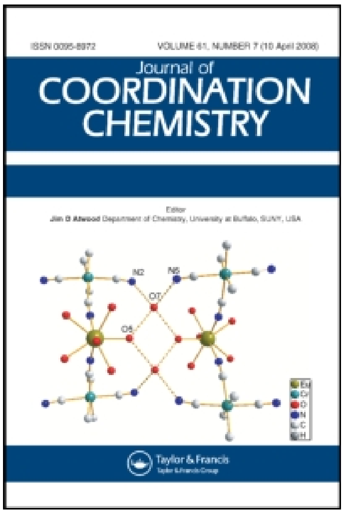

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Synthesis and X-ray single crystal structures of $[Mo(S_2CNⁿBu_2)_4]$ and $[Mo_2S_4(S_2CNⁿBu_2)_2].1/2\ H_2O$

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Synthesis and X-ray single crystal structures of $[Mo(S_2CN^nBu_2)_4]$ and $[Mo_2S_4(S_2CN^nBu_2)_2].1/2\ H_2O$

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The molybdenum dithiocarbamato complexes $[Mo(S_2CN^nBu_2)_4]$ (**1**), $[Mo_2S_4(S_2CN\ ^nBu_2)_2$. $1/2H_2O$ (**2**) have been synthesized and characterized. Single crystal X-ray studies of (**1**) showed that molybdenum atom is coordinated to eight sulfur atoms in dodecahedron geometry and the bond lengths and bond angles fall within the range of values expected. In (**2**) the molybdenum atoms are coordinated to five sulfur atoms in a distorted square pyramid.

Keywords: Molybdenum; Dithiocarbamates; Crystal structures; Precursors; Molybdenum sulfide

1. Introduction

A series of tetranuclear $[Mo_4S_4(R_2NCS_2)_6]$ complexes were prepared by Coyle and co-workers using a 'self-assembly' route as well as by synthesis from well-defined molecular building blocks [1]. The reactions of $[MCp^*Cl_4]$ ($M = Mo$, W; $Cp^* = \eta^5\text{-}C_5Me_5$) with salts of N,N –diethyldithiocarbamato [Et_2dtc] and O,O′-diethyldithiophosphato [Et_2dtp] anions yielded the paramagnetic metal (V) complexes [$MCp^*Cl_3(Et_2$dtc)] and [$MCp^*Cl_3(Et_2$dtp)] ($M = Mo$, W), respectively [2]. Hydrolytic oxidation of both dithiocarbamate-molybdenum complexes with aqueous hydrogen peroxide leads to η^2-coordinated peroxo compounds [MoCp*Cl(O-O)O], which could also be obtained from $[MoCp^*Cl_4]$.

The synthesis and characterization of tetrabutylammonium N,N-diethyldithiocarbamato-*bis*(maleonitriledithiolato)molybdate(IV) and its tungstenate(IV) analogue have also been reported [3]. This preparation was achieved by refluxing $(Bu_4N)[M(CO)_5I]$ with NH_4(Et_2dtc) for 5 min followed by addition of sodium maleonitriledithiolate which resulted in the evolution of CO. On completion of this reaction, I_2 and NH_4(Et_2dtc) were added, and after reflux for 30 min, dark violet crystals formed for the molybdenum complex and dark brown crystals for tungsten.

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A dithiocarbamato compound containing a cubane-like cluster with six molybdenum-molybdenum bonds was prepared by refluxing $[Mo_2(S_2CN(C_2H_5)_2)_6]$ in toluene for 20 h. Black crystals were obtained on cooling to 60°C[4]. Earlier, Brown *et al.*, prepared $[Mo_2(S_2CN(C_2H_5)_2)_6]$ by refluxing freshly sublimed tricarbonyl (η^6-1,3,5,-cycloheptatriene)molybdenum with tetraethyl thiuram disulfide [5].

Syntheses were also reported for a number of oxo- and sulfide-bridged molybdenum(V) complexes with the 1,1-dithiolate ligands N,N-diethyldithiocarbamato (dtc), and diisopropyldithiophosphinato (dtp). The bridge and terminal oxo groups in dtc were sequentially replaced by sulfide in the binuclear core to yield all members of a single family from $[Mo_2O_4(dtc)_2]$ to $[Mo_2S_4(dtc)_2]$ [6].

Herein, we report the synthesis and single crystal X-ray characterization of molybdenum dithiocarbamato complexes $[Mo(S_2CN\ {}^nBu_2)_4]$ (**1**) and $[Mo_2S_4(S_2CN^nBu_2)_2 \cdot 1/2H_2O$ (**2**). Preliminary deposition results show that these complexes have potential as single source precursors for the growth of Mo_xS_y thin films and nanoparticles.

2. Experimental

2.1. *[Mo(S₂CNⁿBu₂)₄] (1)*

$Mo(CO)_6$ (3.96 g, 15 mmol) and dibutylthiuram disulfide (12.26 g, 30 mmol) were added together and refluxed for 3 h in deoxygenated acetone (100 mL) [6]. The solution was cooled to room temperature and the volume of acetone was reduced under vacuum to give red brown crystals which were then filtered. The solid was washed with deoxygenated pentane and then dried under vacuum. Yield: 80%.

Elemental analysis: Expected C: 47.3, H: 7.9, N: 6.1, S: 28.1% Found: C 47.4, H: 8.0, N: 6.1, S: 28.2%. Selected IR data (FTIR) v/cm^{-1}: C-N 1500 (s), C-S 1143 (m) CS_2 992 (m).

2.2. *Preparation of [Mo₂S₄(S₂CN ⁿBu₂)₂] (2)*

$[Mo_2O_4(S_2CN^nBu\ {}_2)_2]$ (0.60 g, 0.91 mmol) and P_4S_{10} (0.20 g, 0.45 mmol) were refluxed in xylene (35 mL) for 3 h. The resulting solution was filtered hot and the red-orange precipitate collected when the solution cooled to room temperature. The precipitate was filtered off and washed with ether (20 mL). Yield: 45%. Elemental analysis: Expected C: 29.7, H: 5.0, N: 3.8% Found: C: 29.8, H: 4.9, N: 3.8%; Selected IR data (FTIR) v/cm^{-1}: $Mo=S$ 589 (vs)

2.3. *Single-crystal X-ray diffraction study*

Suitable crystals of (**1**) were obtained on cooling the reaction mixture to room temperature whereas the crystals for single-crystal diffraction techniques of (**2**) were obtained by slow diffusion process with DCM/hexane at room temperature. Single crystal structure determinations were carried out using graphite monochromoted Mo–K_α radiation ($\lambda = 0.71703$ Å) on a Bruker APEX CCD diffractometer for both complexes. The structures were solved by direct methods and refined by full-matrix least squares on F^2. [7] All calculations were carried out using the SHELXTL package [8]. In each compound, the asymmetric unit consists of half the molecule, with the other half generated by rotation about a two-fold axis. In (**2**), one n-Bu group is disordered over 2 sites whose occupancy was constrained to sum to unity; restraints were used to define the geometry of this group. A water molecule at 0.25 occupancy was also found. The non-hydrogen atoms were refined with anisotropic atomic displacement parameters except for the partially occupied atoms in (**2**). Hydrogen atoms bonded to carbon were placed in calculated positions, assigned isotropic thermal parameters and allowed to ride on their parent carbon atoms; those bonded to the partially occupied water molecule in (2) were omitted.

3. Results and Discussion

Dithiocarbamato complexes of molybdenum $[Mo(S_2CN\ {}^nBu_2)_4]$ (**1**) and $[Mo_2S_4(S_2CN\ {}^nBu_2)_2.1/2H_2O$ (**2**), were synthesized by refluxing a mixture of $Mo(CO)_6$ with dibutylthiuram disulfide, and $Mo_2O_4(S_2CN^nBu_2)_2$ with P_4S_{10}, respectively. Both complexes are crystalline colored solids soluble in most organic solvents. They are stable at room temperature for a period of months which makes them attractive as precursors for the deposition of molybdenum sulfide thin films and nanoparticles.

3.1. *X-ray single crystal structures of $[Mo(S_2CN^nBu_2)_4]$ and $[Mo_2S_4(S_2CN^nBu_2)_2].1/2\ H_2O$*

The molecular structures of (**1**) and (**2**) are shown in Figures 1 and 2, respectively. Crystallographic data and structure refinement parameters for (**1**) and (**2**) are in Table 1. Selected bond distances and angles are given in Tables 2 and 3 for (**1**) and (**2**), respectively.

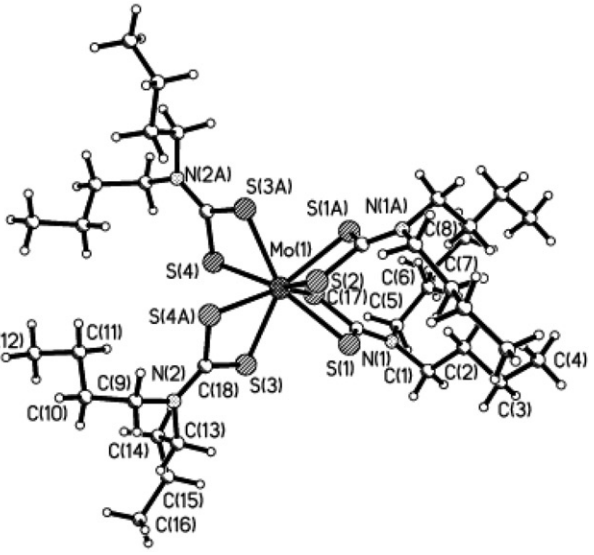

Figure 1. X-ray crystal structure of $[Mo(S_2CN^nBu_2)_4]$.

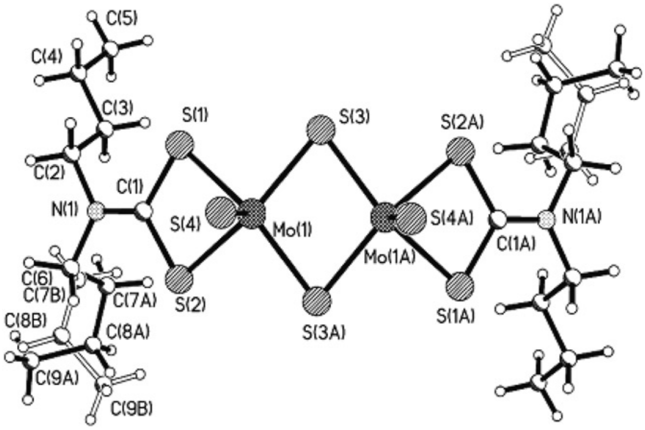

Figure 2. The molecular structure of $[Mo_2S_4(S_2CN^nBu_2)_2]$ showing the disordered n-Bu groups.

Table 1. Crystallographic data and structure refinement parameters for **(1)** and **(2)**.

Compound	$[Mo(S_2CN^nBu_2)_4]$	$[Mo_2S_4(S_2CN^nBu_2)_2] \cdot 1/2\ H_2O$
Empirical formula	$C_{36}H_{72}MoN_4S_8$	$C_{18}H_{37}Mo_2N_2O_{0.50}S_8$
Formula weight	913.40	737.86
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
Unit Cell Dimensions (Å, °)		
a	19.196(2) Å	17.923(2) Å
b	18.361(2) Å	22.178(2) Å
c	16.234(3) Å	8.2829(8) Å
α	90°	90°
β	125.624(4)°	112.121(2)°
γ	90°	90°
Volume	4651.0(11) $Å^3$	3050.2(5) $Å^3$
Z	4	4
Calculated density	1.304 $Mg\,m^{-3}$	1.607 $Mg\,m^{-3}$
Absorption coefficient	0.670 mm^{-1}	1.382 mm^{-1}
F(000)	1944	1500
Crystal size	0.20 × 0.10 × 0.05 mm	0.35 × 0.30 × 0.30 mm
θ range for data collection	1.71 to 28.32 °	1.53 to 26.37 °
Limiting indices	$-25 \leq h \leq 21$, $-23 \leq k \leq 23$, $-21 \leq l \leq 20$	$-22 \leq h \leq 22$, $-27 \leq k \leq 27$, $-10 \leq l \leq 10$
Reflections collected	14226	12054
Unique reflections	5368 [*R*(int) = 0.0878]	3132 [*R*(int) = 0.0220]
Completeness to θ	28.32 92.4%	26.37 100.0%
Absorption correction	None	Semi-empirical from equivalents
Max. and min. transmission	0.9673 and 0.8776	0.6818 and 0.6433
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5368/0/226	3132/9/139
Goodness-of-fit on F^2	0.802	1.088
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0442$, $wR_2 = 0.0736$	$R_1 = 0.0342$, $wR_2 = 0.0912$
R indices (all data)	$R_1 = 0.0889$, $wR_2 = 0.0823$	$R_1 = 0.0359$, $wR_2 = 0.0923$
Largest diff. peak and hole	0.830 and −0.804 $e.A^{-3}$	1.637 and −0.690 $e.A^{-3}$

Table 2. Selected bond lengths (Å) and angles (°) for $[Mo(S_2CN^nBu_2)_4]$.

Mo(1)–S(2A)	2.527(10)
Mo(1)–S(3)	2.529(9)
Mo(1)–S(1)	2.537(10)
Mo(1)–S(4)	2.539(10)
S(3)–Mo(1)–S(4A)	67.04(3)
S(2)–Mo(1)–S(1)	68.11(3)

Table 3. Selected bond lengths (Å) and angles (°) for $[Mo_2S_4(S_2CN^nBu_2)_2]$.

Mo(1)–S(4)	2.106(9)
Mo(1)–S(3)	2.305(8)
Mo(1)–S(3A)	2.312(8)
Mo(1)–S(2)	2.446(8)
Mo(1)–S(1)	2.461(9)
Mo(1)–Mo(1A)	2.809(6)
S(2)–Mo(1)–S(1)	71.21(3)
S(3)–Mo(1)–S(3A)	101.31(3)
S(3)–Mo(1)–S(1)	83.61(3)
S(3A)–Mo(1)–S(2)	82.35(3)

The structure of (**1**) shows that the molybdenum is coordinated to eight sulfur atoms from the dithiocarbamate ligands in approximately dodecahedral coordination [9]. The Mo–S bond lengths can be divided into two groups of tetrahedral geometries; (a) sulfur atoms (S3(a), S2(a), S2, S3) with a mean bond length of 2.53 Å and (b) sulfur atoms (S4(a), S4, S1, S1(a)) with a mean bond length of 2.538 Å. In related studies it has been suggested that this difference in bond length is due to variations in ligand–ligand repulsions rather than metal–ligand $p\pi$-$d\pi$ bonding; there are no significant differences in C–S bond lengths. [6, 9–11] The mean Mo–S bond lengths of compound 2.53 (13) Å are similar to those reported for $[Mo(dtc)_4]Cl$, [12] $[Mo(dtc)_4]I_3$, [13] and $[Mo(dtc)_4](Cl\cdot H_2O)\cdot xCHCl_3$ [14] which are 2.52 (17), 2.52 (26) and 2.52 (10) Å respectively.

The structure of (**2**) (Figure 2) shows that each molybdenum is bonded to two bridged sulfur atoms S(3) and S(3A), one terminal sulfur S(4) and two sulfur atoms S(1) and S(2) from the dithiocarbamato ligand in a distorted square pyramidal geometry. The average S(3)-Mo-S(3A) and Mo(1)-S(3A)-Mo(1A) bond angles of 101.31(3) and 74.99(3)° are similar to those found in related complexes [15,16]. The Mo-S terminal bond length of 2.11(9) Å is more similar to 2.09(12) Å for $[Mo_2S_4(S_2CNEt_2)_2]$ than 1.94(10) Å for $[Mo_2S_4(S_2CN^nBu_2)_2]$. The Mo–S bond distances from the dithiocarbamato ligand are shorter than the reported single bond lengths of *ca.* 2.50(11) Å in $[Mo(dtc)_4]Cl$, [12] $[Mo(dtc)_4](Cl.H_2O)\cdot xCHCl_3$, [14] and $[Mo(dtc)_4]I_3$ [13]. The bond lengths are also less than the observed Mo-S bond distances for 1,2-dimercaptoethane, [17] and cysteine [18] ligands.

Preliminary results from the deposition studies by the Aerosol Assisted Chemical Vapour Deposition (AACVD) method showed that these complexes have the potential as precursors for the deposition of molybdenum sulfide thin films and nanoparticles.

Supplementary data

Crystallographic data for the structure have been deposited with the Cambridge Data Centre as supplementary publication CCDC reference numbers 263010 (1) and 649490 for (2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223 336 033; Email: deposit@ccdc.cam.ac.uk).

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