Synthesis, Spectroscopic and X-Ray Structure Characterisation of Bis(tetramethylammonium) and Bis(tetra-*n*-butylammonium) Tetrathiomolybdates

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The new tetraalkylammonium tetrathiomolybdates $(Me_4N)_2[MoS_4]$ (**1**) and $(nBu_4N)_2[MoS_4]$ (**2**) were prepared *via* a direct salt substitution using $(NH_4)_2[MoS_4]$ as starting material. Compound **1** crystallises in the non-centrosymmetric orthorhombic space group $P2_12_12_1$ with $a = 8.9233(4)$, $b = 15.5210(9)$ and $c = 37.255(3)$ Å. Compound **2** crystallises in the orthorhombic space group $Fdd2$ with $a = 28.9142(18)$, $b = 35.7811(10)$ and $c = 15.6774(17)$ Å. The structures of both compounds consist of slightly distorted $[MoS_4]^{2-}$ tetrahedra and tetraalkylammonium cations which are packed in different ways. Single crystals of $(Et_4N)_2[MoS_4]$ (**3**) were also investigated giving the lattice parameters $a = 14.0346(7)$ and $c = 12.5143(8)$ Å. A very strong disorder prevented a successful structure refinement and only the anion and one cation could be located. It is remarkable that the disorder of parts of the alkyl groups decreases with increasing chain length, in correlation with the IR and Raman vibrations of the $[MoS_4]^{2-}$ tetrahedron showing a slight shift to lower energy with increasing alkyl chain length. The most prominent IR band of $[MoS_4]^{2-}$ is broad but not split, indicating that the distortion of the tetrahedra is small.

Key words: Crystal Structure, Tetrathiomolybdates, IR and Raman Spectroscopy

Introduction

The synthesis of molybdenum(IV) disulfide has been performed by a wide variety of methods leading to diverse particle sizes ranging from well developed crystals, powders, meso- or microporous materials to nanoparticles for a broad spectrum of purposes: solid lubricants for fireproof products [1], space technologies [2], base materials for semiconductor nanoclusters [3], electrode materials for photoelectrochemical solar cells [4], catalysts for electrochemical hydrogen evolution reactions [5], and the deep hydrodesulfurisation (HDS) of refinery streams [6]. Several research groups have observed that molybdenum sulphide compounds containing carbon (MoS_2-C) show enhanced properties with respect to electrical conductivity [7], tribology [8], morphology [9, 10], and improved catalytic activity for hydrotreating reactions [11]. The role of structurally incorporated carbon for the activity of a HDS catalyst was investigated and the results of a profound study gave evidences that a critical carbon content is essential for a high performance of such catalysts [12].

In a previous report we presented results of the synthesis of MoS_2 catalysts by the thermal decomposition of tetraalkylammonium tetrathiomolybdates, and we demonstrated that for MoS_2-based catalysts the carbon content of the active material can be determined by the carbon content of the $(R_4N)_2MoS_4$ (R = organic substituents) precursors [13]. In the meantime, nine thiomolybdates have been synthesised by our group: piperazinium, tris(2-aminoethyl)aminium, tetrapropylammonium [14], 1,3-propanediammonium, tetramethylethylenediammonium [15], 1,4-butanediammonium [16], bis[(±)-*trans*-2-aminocyclohexylammonium], *trans*-cyclohexane-1,4-diammonium [17], and bis(methylammonium) tetrathiomolybdate [18]. Only one of these compounds contains a tetraalkylammonium ion for charge balancing [14]. The present contribution is part of our ongoing investigations aimed at the synthesis of active and efficient MoS_2 and WS_2 catalysts, and its Ni/Co

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promoted versions. The full characterisation of the precursor materials and the understanding of the chemical reactivity require the knowledge of the crystal structures. The syntheses, crystal structures and spectroscopic data of two new tetraalkylammonium tetrathiomolybdates $(R_4N)_2MoS_4$ (R = methyl and n-butyl) are presented. For R = ethyl some preliminary results are also reported.

Experimental Section

Synthesis

The synthesis of tetraalkylammonium salts $(R_4N)_2[MoS_4]$ by different preparative strategies was reported by several groups [19, 20]. In the present work, a slightly modified version was used and crystals were grown from very dilute solutions. The amines and the solvents were used as obtained from commercial sources. $(NH_4)_2[MoS_4]$ was prepared as reported by McDonald [19]. For the synthesis of the tetramethyl and tetraethyl thiomolybdates freshly prepared $(NH_4)_2[MoS_4]$ (1.4 mmol) was dissolved in water (30 mL) and stirred. $(R_4N)Br$ (2.8 mmol) was dissolved in a solution of NaOH (2.8 mmol) in 10 mL of water and stirred. The two solutions were mixed and stirred for 30 min. The solutions were kept undisturbed over ice, and red crystals precipitated overnight. The solids were filtered and washed with cold water and ethanol. The yield was about 80 % for both compounds. The compounds are stable in air for a long time period. The tetra-*n*-butylammonium thiomolybdate was synthesised using freshly prepared $(NH_4)_2[MoS_4]$ (0.7 mmol) which was dissolved in water (10 mL). An aqueous solution of $(nBu_4N)Br$ (1.4 mmol, 20 mL water) was added and the mixture was stirred for 30 min. Red crystals precipitated overnight which were stored under static vacuum over P_2O_5 (yield 80 %).

Characterisation

A CHN-O RAPID combustion analyser from Heraeus was used to determine the content of C, H, N, and S, using zinc sample holders with 2 – 3 mg samples, heated up to 1000 °C under oxygen atmosphere. Compound **1**: calcd. C 25.8, H 6.5, N 7.5, S 34.5; found C 25.9, H 6.5, N 7.5, S 34.5; compound **2**: calcd. C 54.2, H 10.2, N 3.9, S 18.1; found C 53.2, H 9.9, N 3.9, S 18.4; compound **3**: calcd. C 39.6, H 8.2, N 5.8, S 26.5; found C 39.1, H 8.1, N 5.7, S 26.1. Far IR spectra (80 – 500 cm^{-1}) were measured on a Bruker IFS 66 spectrometer in pressed polyethylene disks. MIR spectra (450 – 3000 cm^{-1}) were recorded with an ATI Mattson Genesis spectrometer. The samples were ground with dry KBr into fine powders and pressed into transparent pellets. Raman spectra were measured from 100 to 3500 cm^{-1} with a Bruker IFS 66 Fourier Transform Raman spectrometer.

Table 1. Technical details of data acquisition and selected refinement results for **1** – **2**.

Compound	**1**	**2**
Formula	$C_8N_2H_{24}MoS_4$	$C_{32}N_2H_{72}MoS_4$
Formula weight, g mol^{-1}	372.47	709.10
Space group	$P2_12_12_1$	$Fdd2$
Temperature, K	293	293
Wavelength, Å	0.71073	0.71073
a, Å	8.9233(4)	28.9142(18)
b, Å	15.5210(9)	35.7811(10)
c, Å	37.255(3)	15.6774(17)
V, $Å^3$	5159.8(5)	16220(2)
Z	12	16
μ, mm^{-1}	1.23	0.55
$F(000)$, e	2304	6144
D_{calc}, g cm^{-3}	1.438	1.162
Crystal size, mm^3	$0.15 \times 0.12 \times 0.12$	$0.6 \times 0.8 \times 0.6$
2θ range, deg	3 – 45	5 – 56
Collected reflections	32907	31396
Unique reflections	6589	9645
Data ($F_o \geq 4\sigma(F_o)$)	5482	6615
R_{int}	0.0436	0.0987
Parameters refined	398	353
Goodness of fit	1.083	0.994
Flack parameter x	0.0751(4)	
BASF parameter	0.455(1)	
$R1$ ($F_o \geq 4\sigma(F_o)$)[a]	0.0328	0.0502
$wR2$ (all unique data)	0.0865	0.1064
$\Delta\rho$, e $Å^{-3}$	−0.455/0.414	−0.4544/0.414

[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

Structure refinement details

Single crystal investigations of the compounds were performed using an Imaging Plate Diffraction System (IPDS-1) [21] with monochromated MoK_α radiation (λ = 0.71073 Å). All structures were solved by Direct Methods using SHELXS-97 [22] and the refinements were carried out against F^2 using SHELXL-97 [23]. The data were corrected for Lorentz polarisation, and absorption effects. The crystal of compound **1** was racemically twinned, and therefore a twin refinement was performed (BASF parameter: 0.45(4)). All non-hydrogen atoms were refined anisotropically except for the methyl groups of two of the six tetramethylammonium cations which exhibit a positional disorder. All hydrogen atoms were placed in ideal geometry and were refined using a riding model. Fore compound **3** the absolute structure was determined be to in agreement with the selected setting (Flack parameter $x = -0.07(4)$). The structure of compound **3** was solved in the space group $P4/n$ and the anion as well as one cation could be located easily, but the second cation was heavily disordered and no reliable structural model could be found.

Technical details of the data acquisitions and some refinement results are summarised in Table 1. Lists of selected bond lengths are given in Tables 2 and 3. Crystallographic data (excluding structure factors) for the structures reported

Table 2. Selected geometric parameters (Å, deg) for $(Me_4N)_2[MoS_4]$ (**1**).

Mo(1)–S(1)	2.175(2)	Mo(2)–S(7)	2.177(3)
Mo(1)–S(2)	2.166(3)	Mo(2)–S(8)	2.172(2)
Mo(1)–S(3)	2.182(2)	Mo(3)–S(12)	2.177(3)
Mo(1)–S(4)	2.178(3)	Mo(3)–S(9)	2.182(2)
Mo(2)–S(5)	2.177(3)	Mo(3)–S(10)	2.183(2)
Mo(2)–S(6)	2.159(3)	Mo(3)–S(11)	2.186(2)
S(1)–Mo(1)–S(4)	110.87(12)	S(6)–Mo(2)–S(5)	109.41(15)
S(2)–Mo(1)–S(3)	109.86(13)	S(8)–Mo(2)–S(5)	110.29(13)
S(1)–Mo(1)–S(3)	109.64(10)	S(7)–Mo(2)–S(5)	109.32(15)
S(4)–Mo(1)–S(3)	108.84(11)	S(9)–Mo(3)–S(10)	110.12(12)
S(2)–Mo(1)–S(1)	108.96(12)	S(9)–Mo(3)–S(11)	109.22(10)
S(2)–Mo(1)–S(4)	108.65(12)	S(10)–Mo(3)–S(11)	108.90(11)
S(6)–Mo(2)–S(8)	109.44(11)	S(12)–Mo(3)–S(9)	110.06(9)
S(6)–Mo(2)–S(7)	109.53(12)	S(12)–Mo(3)–S(10)	108.18(10)
S(8)–Mo(2)–S(7)	108.85(11)	S(12)–Mo(3)–S(11)	110.34(11)

Table 3. Selected geometric parameters (Å, deg) of $(n\text{Bu}_4\text{N})_2[MoS_4]$ (**2**).

Mo(1)–S(1)	2.1792(14)	Mo(1)–S(3)	2.1898(15)
Mo(1)–S(2)	2.2047(13)	Mo(1)–S(4)	2.1950(13)
S(1)–Mo(1)–S(2)	110.58(6)	S(3)–Mo(1)–S(4)	108.62(6)
S(1)–Mo(1)–S(3)	109.58(8)	S(3)–Mo(1)–S(2)	110.05(5)
S(1)–Mo(1)–S(4)	107.85(6)	S(4)–Mo(1)–S(2)	110.12(5)

in this paper were deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 626635 (**1**), CCDC 626636 (**2**). Copies of the 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

For $(Me_4N)_2[MoS_4]$ (**1**) some crystallographic data have been published previously [24], and it was claimed that the material crystallises in space group *Pnam*. Unfortunately, no atomic coordinates and no *R* values have been deposited in the CCDC data base [25]. Furthermore, a comparison of the lattice parameters with that of **1** shows that there is a strong indication that the authors have overlooked reflections which lead to tripling of one unit cell axis. According to the present study, compound **1** crystallises in the orthorhombic space group $P2_12_12_1$, which was also observed for the analogous tungsten compound [27]. The unit cell parameters of the analogous tungsten compound are slightly larger than those of the present material which is caused by the differences of the ionic radii of W(VI) and Mo(VI). There are three crystallographically independent anions per asymmetric unit with no imposed symmetry (Table 2). The Mo(1)–S distances in the first anion

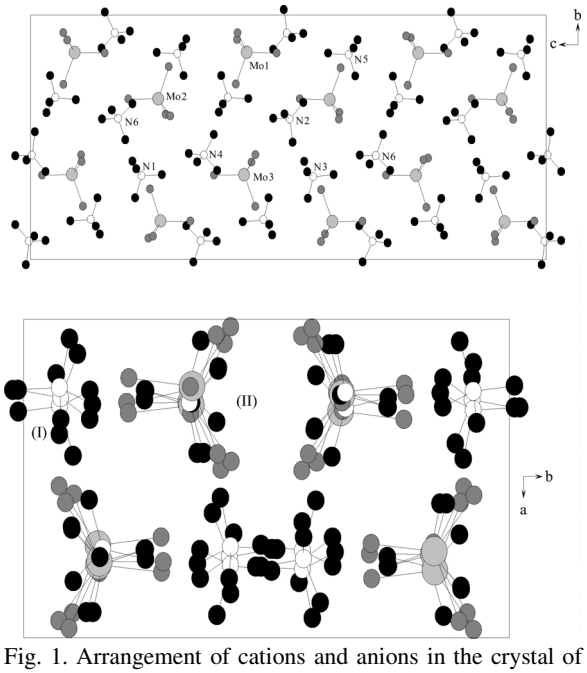

Fig. 1. Arrangement of cations and anions in the crystal of compound **1** viewed along the [100] (top) and along the [001] direction (bottom). The numbers (I) and (II) denote the two different rods formed either by cations alone (I) or by alternating cations and anions (II).

range from 2.165(3) to 2.182(2) Å with an average of 2.173(2) Å. The Mo(1)S_4 tetrahedron is slightly distorted with S–Mo(1)–S angles between 108.66(12) and 110.85(12)° (average: 109.75(12)°). The Mo(2)–S bonds are between 2.178(3) and 2.186(2) Å (mean value: 2.182(2) Å) with S–Mo(2)–S angles from 108.24(11) to 110.33(12)° (average: 109.28(12)°). In the third anion, the Mo(3)–S bond lengths range from 2.158(3) to 2.178(3) Å (average: 2.168(3) Å) and the S–Mo(3)–S angles are between 108.86(12) and 110.27(13)° (average: 109.56(12)°) (see also Table 2). The differences Δ between the longest and shortest Mo–S bond lengths amount to 0.016, 0.018, and 0.009 Å for Mo(1), Mo(2), and Mo(3), respectively. These small values as well as the S–Mo–S angles indicate that the tetrahedral geometry is only moderately distorted.

Three methyl groups of the cations show a positional disorder with 50 % occupancies for two positions in cation N(1), while for cation N(2) these groups exhibit occupancies of 60 % : 40 %. Fig. 1 shows two different views of the arrangement of cations and anions. Looking along [001] two different types of rods are seen. Type (I) is composed solely of cations, and

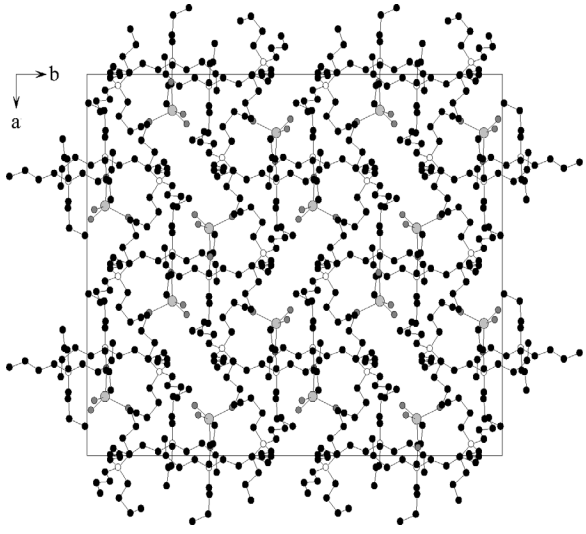

Fig. 2. Arrangement of the cations and anions in the structure of compound **2**.

in type (II) cations and anions alternate. Along [010] these rods are arranged with the sequence ... (II)–(II)–(I)–(I).... The view along [010] reveals a layer-like arrangement of cations an anions.

$(n\mathrm{Bu_4N})_2[\mathrm{MoS_4}]$ (**2**) crystallises in the orthorhombic space group *Fdd*2 with a = 28.9142(18), b = 35.7811(10), and c = 15.6774(17) Å. The asymmetric unit contains one crystallographically independent anion and two independent cations. The $\mathrm{MoS_4}$ tetrahedron shows a moderate distortion which is slightly more pronounced than that for compound **1** (S–Mo–S angles: 107.85(6) – 110.58(6)°, Table 1, Mo–S bond lengths: 2.1792(14) – 2.2047(13) Å, Table 3) with a corresponding value for Δ of 0.0255 Å. No positional disorder was observed in this structure. In Fig. 2 the arrangement of anions and cations viewed along [001] is displayed. Eight cations are grouped to form pockets which host the anions.

Compound **3** crystallises in a primitive tetragonal space group with cell parameters a = 14.0346(7) and c = 12.5143(8) Å. It is a polymorph of the compound which was obtained by crystallisation in acetonitrile and ether [28]. Normally, thiotungstates and thiomolybdates with the same cation are isostructural. In the present case the Mo compound is not isostructural with the W analogue because the latter was reported to crystallise in space group $P2_1/n$ [27].

The compounds were further characterised by IR and Raman spectroscopy. In addition IR and Raman spectra were also recorded for the propyl compound [14]. The absorptions around 3000 $\mathrm{cm^{-1}}$ are assigned to the C–H stretching vibrations with a shift to lower wave numbers with increasing chain length. Between 900 and 1500 $\mathrm{cm^{-1}}$ further bands of the aliphatic chains and the C–N vibrations are seen [29, 30]. For a free tetrahedral $\mathrm{MoS_4}$ anion four characteristic bands $\nu_1(\mathrm{A_1})$, $\nu_2(\mathrm{E})$, $\nu_3(\mathrm{F_2})$, and $\nu_4(\mathrm{F_2})$ are expected [31, 32] of which ν_3 and ν_4 are IR active and all others are Raman active [33]. The strong bands observed in the 400 – 510 $\mathrm{cm^{-1}}$ region of the IR spectra (Fig. 3) are assigned to the triply degenerated asymmetric vibrations ν_3 of the $\mathrm{MoS_4}$ tetrahedra.

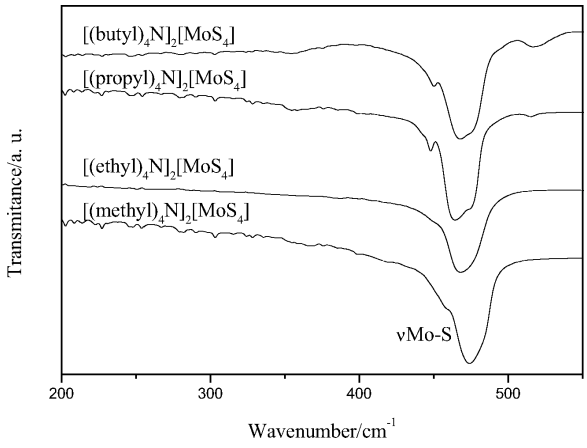

Fig. 3. Infrared spectra of tetraalkylammonium thiomolybdates in the region of Mo–S vibrations.

In the same way as observed for the tungsten analogues a slight shift of the absorption maximum to lower wave numbers with increasing alkyl chain length is observed: Me (474 $\mathrm{cm^{-1}}$) > Et (467 $\mathrm{cm^{-1}}$) > *n*Pr (464 $\mathrm{cm^{-1}}$) < *n*Bu (467.8 $\mathrm{cm^{-1}}$). A similar observation was reported earlier for R = Me and *n*Bu [20] and was explained on the basis of decreasing electropositivity with increasing chain length, but such an effect was not found when R was pentyl or hexyl [34]. However the tendency in the present series of compounds is not regular because for R = *n*Bu the band maximum is comparable with that for R = Et. It therefore appears that the positional disorder affects the absorption maximum leading to the observed trend. The sharp bands at about 450 $\mathrm{cm^{-1}}$ in the spectra of the *n*Pr and *n*Bu compounds are due to the organic part of the compounds. As expected the peak maxima of the asymmetric vibrations of the molybdenum compounds occur at higher wave numbers as compared to the tungsten samples.

The difference between the longest and shortest Mo–S distance is an important factor which may be considered as a measure for the distortion of the $[MoS_4]^{2-}$ tetrahedron. In a recent report [35] the structural and spectroscopic properties of 14 tetrathiotungstate complexes were analysed. One interesting result of the analysis is that a critical value for Δ of about 0.03 Å is required to see a splitting of W–S vibrations in the IR spectra. In many tetrathiotungstates and tetrathiomolybdates large Δ values are caused by N–H···S interactions. The analysis also revealed that the number and strength of these interactions determine the distortion of the WS_4 tetrahedron. For the fully alkylated ammonium ions no such hydrogen bonding interactions are possible and consequently the Δ values lie below the above mentioned limit, and only broad absorptions are seen in the IR spectra. A short comment should be made concerning the decrease of the positional disorder of the alkyl groups with increasing size of these molecules. The atomic volume for the non-H atoms decreases from 28.7 $Å^3$ for R = methyl to 25.5 $Å^3$ for R = *n*-butyl, *i. e*., larger alkyl chains support a more dense packing which reduces the positional disorder.

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