

# Triangular $W_3S_7^{4+}$ and $W_3S_4^{4+}$ complexes

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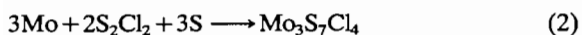
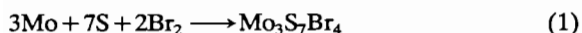
(Received January 23, 1990; revised April 9, 1990)

## Abstract

Methods for the synthesis of triangular thiohalogenide complexes of tungsten  $W_3S_7X_4$  ( $X=Cl, Br$ ) proceeding from metallic tungsten or  $WS_3$  have been developed. Ways have been found for converting these polymeric complexes to triangular  $W_3S_7X_6^{2-}$  complexes which preserve the architecture of the  $W_3(\mu_3-S)(\mu_2-S_2)_3^{4+}$  cluster fragment. Heating  $W_3S_7X_4$  in a  $PPh_4X$  melt or in concentrated acids  $HX$  in the presence of  $Et_4NX$  afforded  $PPh_4^+$  and  $Et_4N^+$  salts of  $W_3S_7X_6^{2-}$  ( $X=Cl, Br$ ). The structure of  $(Ph_4P)_2W_3S_7Br_6$  (**III**) was established by X-ray diffraction analysis. The crystals of **III** are orthorhombic,  $a=18.082(2)$ ,  $b=25.834(3)$ ,  $c=27.370(2)$  Å,  $Z=8$ ,  $Pbca$ ,  $R(R_w)=0.049$  (0.055). The  $Et_4N^+$  salt of  $W_3^{34}S_7Br_6^{2-}$  has been obtained and a calculation of the normal vibrations has been performed for  $W_3S_7Br_6^{2-}$ . Interaction of  $W_3S_7Br_4$  with a KNCS melt or an aqueous solution of  $(NH_4)_2S_x$  involves transformation of the cluster fragment  $W_3S_7^{4+}$  to a  $W_3S_4^{4+}$  fragment to produce  $W_3S_4(NCS)_9^{5-}$  and  $W_3S_4(S_4)_3(NH_3)_3^{2-}$  complexes. The structure of  $(NH_4)(H)(H_2O)_3W_3S_{16}(NH_3)_3$  (**VI**) was established by X-ray diffraction analysis. The crystals of **VI** are trigonal,  $a=12.508(1)$ ,  $c=10.112(1)$  Å,  $Z=2$ ,  $P31c$ ,  $R(R_w)=0.029$  (0.033).

## Introduction

The triangular thiohalogenide complexes of Mo were obtained over 20 years ago upon heating  $MoX_n$  ( $n=2, 3$ ) with sulfur at 350–450 °C [1, 2]. In 1986 we proposed new routes for the synthesis of these compounds proceeding from metallic molybdenum or  $MoS_3$  (eqns: (1)–(3)) [3].



Recent works indicated that the readily available  $Mo_3S_7X_4$  complexes are synthons for the preparation of  $Mo_3S_7^{4+}$  [4–8] and  $Mo_3S_4^{4+}$  [5, 9, 10] complexes. The chemistry of the triangular thiocomplexes of tungsten is less developed than that of the analogous thiocomplexes of Mo [11, 12] and it was therefore of interest to study the possibility of obtaining  $W_3S_7X_4$  complexes and then to study their chemical properties

with the aim of the synthesis of  $W_3S_7^{4+}$  and  $W_3S_4^{4+}$  complexes.

In 1989 Cotton and co-workers prepared  $W_3S_7Br_4$  from the elements at 425 °C and determined the structure of this polymeric complex  $W_3(\mu_3-S)(\mu_2-S_2)_3Br_2Br_{4/2}$  [10]. In the same year Saito and co-workers obtained  $W_3S_7Cl_4$  upon heating  $WCl_2$  with sulphur at 300 °C and employed this compound to synthesize the octahedral  $W_6S_8(PEt_3)_6$  complex [13].

In the present work we discuss our results on the synthesis of  $W_3S_7Br_4$  and  $W_3S_7Cl_4$  from metallic tungsten and  $WS_3$ . We employed these polymeric compounds to obtain  $W_3S_7X_6^{2-}$  salts and to prepare  $W_3S_4^{4+}$  complexes –  $W_3S_4(NCS)_9^{5-}$  and  $W_3S_4(S_4)_3(NH_3)_3^{2-}$ .

## Experimental

### Materials and apparatus

Metallic tungsten with an average particle size of 13  $\mu m$  was used in this work. Bromine was distilled over  $P_4O_{10}$ ;  $S_2Cl_2$  over charcoal and sulfur. The

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solvents  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  were distilled over  $\text{P}_4\text{O}_{10}$ . The solution of  $(\text{NH}_4)_2\text{S}_x$  was obtained by saturating a suspension of 20 g sulfur in 200 ml of 25%  $\text{NH}_3$  with  $\text{H}_2\text{S}$  to complete dissolution of sulfur.  $\text{WS}_3$  was obtained by heating  $(\text{NH}_4)_2\text{WS}_4$  under vacuum. The isotope-containing compounds were prepared using sulfur containing 99.95% of  $^{34}\text{S}$  and molybdenum containing 95% of  $^{92}\text{Mo}$  and  $^{100}\text{Mo}$ . All other reagents were used as received.

The IR spectra were recorded in KBr pellets or in polyethylene on a IFS-113 Fourier spectrometer (Bruker). The Raman spectra were obtained on a DFS-24 spectrometer at an angle of  $90^\circ$  using 441.5 and 632.8 nm lines of He–Cd and He–Ne lasers, respectively, for excitation. The UV–Vis spectra were taken with a Specord spectrometer. To measure magnetic susceptibility the Faraday method was used.

Tungsten and sulfur were determined gravimetrically as  $\text{WO}_3$  and  $\text{BaSO}_4$ , respectively. All other analyses were made in the laboratory of microanalysis of the Institute of Organic Chemistry (Novosibirsk). The analytical and spectroscopic data for  $\text{W}_3\text{S}_7^{4+}$  and  $\text{W}_3\text{S}_4^{4+}$  complexes I–VIII are listed in Table 1.

### Syntheses

#### Preparation of $\text{W}_3\text{S}_7\text{Br}_4$ (I)

Tungsten (5.00 g, 27.2 mmol), sulfur (2.03 g, 63.3 mmol) and  $\text{Br}_2$  (0.96 ml, 18.6 mmol) were heated in an evacuated sealed quartz ampoule at  $300^\circ\text{C}$  for 48 h after which the mixture was thoroughly stirred and heated for another 72 h. Then the ampoule was opened, the solid washed with  $\text{CHCl}_3$  and hot benzene and dried under vacuum. Yield: 9.70 g of I, 97%.

$\text{W}_3^{34}\text{S}_7\text{Br}_4$  was obtained from  $^{34}\text{S}$  in an analogous manner.

Complex I was also formed upon heating 2.00 g of  $\text{WS}_3$  and 0.46 ml of  $\text{Br}_2$  at  $300^\circ\text{C}$ .

#### Preparation of $\text{W}_3\text{S}_7\text{Cl}_4$ (II)

$\text{WS}_3$  (2.00 g, 7.14 mmol) and  $\text{PCl}_5$  (1.49 g, 7.14 mmol) were heated in an evacuated sealed ampoule at  $180^\circ\text{C}$  for 6 h. Then the ampoule was opened and the volatile reaction products were removed under vacuum at  $100^\circ\text{C}$ . The solid residue was then sealed in an ampoule and heated for 48 h at  $300^\circ\text{C}$ . Further treatment was as in the previous procedure. Yield: 1.85 g of II, 84%.

#### Preparation of $(\text{PPh}_4)_2\text{W}_3\text{S}_7\text{Br}_6$ (III)

$\text{W}_3\text{S}_7\text{Br}_4$  (5.00 g) was melted together with  $\text{PPh}_4\text{Br}$  (10.0 g) at  $295\text{--}300^\circ\text{C}$  under argon. The cold melt was washed with ethanol to remove  $\text{PPh}_4\text{Br}$  and the solid was extracted with hot acetonitrile. Addition of ether to the solution produced 6.51 g of complex

III (75%), and upon addition of benzene to the same solution the solvate  $\text{III}\cdot\text{C}_6\text{H}_6$  (77%) was formed.

#### Preparation of $(\text{Et}_4\text{N})_2\text{W}_3\text{S}_7\text{Br}_6$ (IV)

$\text{W}_3\text{S}_7\text{Br}_4$  (0.95 g) was heated in 20 ml of concentrated  $\text{HBr}$  in the presence of 2.0 g  $\text{Et}_4\text{NBr}$ . The hot solution was filtered and cooled to  $-5^\circ\text{C}$ . After an overnight standing the red crystalline solid was washed with water, ether and dried under vacuum. Yield: 0.51 g of IV, 38%.

Proceeding from  $\text{W}_3^{34}\text{S}_7\text{Br}_4$ ,  $(\text{Et}_4\text{N})_2\text{W}_3^{34}\text{S}_7\text{Br}_6$  was obtained by an analogous procedure.

#### Preparation of $(\text{Et}_4\text{N})_2\text{W}_3\text{S}_7\text{Cl}_6$ (V)

$\text{WS}_3$  (0.98 g, 1.51 mmol) and  $\text{S}_2\text{Cl}_2$  (0.46 g, 3.41 mmol) were heated at  $320^\circ\text{C}$  for 48 h in an evacuated sealed quartz ampoule. The ampoule was then opened, the solid treated with  $\text{CHCl}_3$  and  $\text{CH}_3\text{CN}$  and dried under vacuum. The brown powder was boiled with 50 ml of concentrated  $\text{HCl}$  in the presence of 2.0 g of  $\text{Et}_4\text{NBr}$ . The red solution was evaporated before the onset of crystallization and kept overnight at  $-5^\circ\text{C}$ . Yield: 0.05 g of complex V, 3%.

#### Reaction of $(\text{Et}_4\text{N})_2\text{W}_3\text{S}_7\text{Cl}_6$ with $\text{Ph}_3\text{P}$

To a solution of  $(\text{Et}_4\text{N})_2\text{W}_3\text{S}_7\text{Cl}_6$  (9.3 mg) in 25 ml of  $\text{CH}_3\text{CN}$  5.9 mg of  $\text{Ph}_3\text{P}$  were added. The initial red colour of the solution immediately changed to greenish-blue. The electronic spectrum of this solution shows a band at 610 nm ( $\epsilon 870$ ) which is in good agreement with the values reported for different  $\text{W}_3\text{S}_4^{4+}$  compounds [13–15].

#### Reaction of $^{92}\text{Mo}$ and $^{100}\text{Mo}$ with S and $\text{Br}_2$

A mixture of  $^{92}\text{Mo}$  (0.15 g),  $^{100}\text{Mo}$  (0.16 g) with  $\text{Br}_2$  (0.18 ml) and S (0.24 g) was heated at  $300^\circ\text{C}$  for 48 h and then treated as described in ref. 3. The IR and Raman spectra of this sample were not a superposition of those of the individual  $^{92}\text{Mo}_3\text{S}_7\text{Br}_4$  and  $^{100}\text{Mo}_3\text{S}_7\text{Br}_4$  [16].

#### Attempt at the preparation $\text{Mo}_x\text{W}_{3-x}\text{S}_7\text{Br}_4$ heterometallic clusters

An equimolar mixture of Mo (0.26 g) and W (0.50 g) or  $\text{WS}_3$  (0.62 g) and  $\text{MoS}_3$  (0.40 g) with stoichiometric quantities of corresponding reagents was heated for 72 h under the conditions identical to those described above for the synthesis of the individual  $\text{W}_3\text{S}_7\text{Br}_4$ . The red–brown solids produced were washed with methylene chloride and hot benzene and dried *in vacuo*.

The vibrational spectra of these solids showed the presence of only homometallic  $\text{Mo}_3\text{S}_7\text{Br}_4$  and  $\text{W}_3\text{S}_7\text{Br}_4$  in both cases.

TABLE 1. Analytical and spectral data for triangular complexes of tungsten

Compound	Colour	Analyses		Spectral data (cm <sup>-1</sup> )
		Found (%)	Calculated (%)	
W <sub>3</sub> S <sub>7</sub> Br <sub>4</sub> (I)	red-brown	W	51.5	IR: 542, 446, 295, 213, 170, 144 Raman: 550, 540, 447, 378, 365, 335, 314, 290, 252, 237, 212, 160, 99
		S	20.6	
		Br	28.8	
W <sub>3</sub> S <sub>7</sub> Cl <sub>4</sub> (II)	red-brown	W	59.3	IR: 560, 550, 442, 372, 318, 297, 265, 234 Raman: 563, 554, 443, 373, 335, 318
		S	23.2	
		Cl	15.6	
(Ph <sub>4</sub> P) <sub>2</sub> W <sub>3</sub> S <sub>7</sub> Br <sub>6</sub> ·C <sub>6</sub> H <sub>6</sub> (III·C <sub>6</sub> H <sub>6</sub> )	red	C	32.3	IR <sup>a</sup> : 453, 309, 287, 230, 209, 183, 167, 154, 148 Raman: 557, 551, 445, 382, 339, 309, 294, 239, 173
		H	2.3	
		W	26.6	
		S	11.2	
		Br	23.5	
		Br	24.0	
(Et <sub>4</sub> N) <sub>2</sub> W <sub>3</sub> S <sub>7</sub> Br <sub>6</sub> (IV)	red	C	12.6	IR and Raman spectra see Fig. 2
		H	2.7	
		N	1.8	
		W	36.4	
		S	14.8	
		Br	31.6	
(Et <sub>4</sub> N) <sub>2</sub> W <sub>3</sub> S <sub>7</sub> Cl <sub>6</sub> (V)	red	C	15.5	IR <sup>a</sup> : 563, 552, 441, 370, 317, 296, 263, 235, 206, 193, 174, 157, 143, 116 Raman: 564, 553, 443, 373, 335, 317, 295, 232, 203, 193, 173
		H	3.1	
		N	2.1	
		H	1.9	
		N	5.6	
		W	46.7	
(NH <sub>4</sub> ) <sub>2</sub> (H)(H <sub>2</sub> O) <sub>3</sub> W <sub>3</sub> S <sub>16</sub> (NH <sub>3</sub> ) <sub>3</sub> (VI)	black	W	46.7	IR: 3420, 3144, 3000, 2800, 1590, 1396, 1228, 692, 461, 445, 425, 321, 283, 232, 217, 170 Raman: 477, 464, 412, 265, 237, 220, 203, 154
		S	43.7	
		C	30.8	
		H	5.5	
		N	10.3	
		W	30.4	
(Et <sub>4</sub> N) <sub>3</sub> W <sub>3</sub> S <sub>4</sub> (NCS) <sub>9</sub> (VII)	green	S	22.4	Electronic spectrum in CH <sub>3</sub> CN: λ (nm) (ε (M <sup>-1</sup> ·cm <sup>-1</sup> )): 625(720), 316(40560), 267(56900), 238(59920) IR <sup>a</sup> (Δν for (Et <sub>4</sub> N) <sub>3</sub> W <sub>3</sub> S <sub>4</sub> <sup>3+</sup> (NCS) <sub>9</sub> ): 478(0), 459(5), 441(11), 343(7), 266(0), 216(0), 178(0) Raman: 436, 345, 289
		C	6.3	
		H	5.8	
		N	6.5	
		W	22.4	
		S	22.3	
C <sub>3</sub> S <sub>3</sub> W <sub>3</sub> S <sub>4</sub> (NCS) <sub>9</sub> (VIII)	green	C	6.3	IR <sup>a</sup> : 2080, 477, 459, 440, 434, 348, 336, 256, 212, 176
		N	6.5	
		S	22.4	

\*Cationic bands in IR and Raman spectra are omitted.

Additionally, the treatment of these solids with HBr/Et<sub>4</sub>NBr lead to a mixture of (Et<sub>4</sub>N)<sub>2</sub>W<sub>3</sub>S<sub>7</sub>Br<sub>6</sub> and (Et<sub>4</sub>N)<sub>2</sub>Mo<sub>3</sub>S<sub>7</sub>Br<sub>6</sub> (Raman); the use of (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> with subsequent treatment with concentrated HCl produced Mo<sub>3</sub>S<sub>7</sub>Cl<sub>6</sub><sup>2-</sup> (identified as the Ph<sub>4</sub>P<sup>+</sup> salt [17]) and W<sub>3</sub>S<sub>4</sub><sup>4+</sup>(aq.) [18, 15]. Melting with KNCS produced only W<sub>3</sub>S<sub>4</sub>(NCS)<sub>9</sub><sup>5-</sup> (see 'Experimental' below).

*Preparation of (NH<sub>4</sub>)(H)(H<sub>2</sub>O)<sub>3</sub>W<sub>3</sub>S<sub>4</sub>(S<sub>4</sub>)<sub>3</sub>(NH<sub>3</sub>)<sub>3</sub> (VI)*

A solution of (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> (20 ml) was added to W<sub>3</sub>S<sub>7</sub>Br<sub>4</sub> (0.22 g) and the mixture was kept for a week at room temperature without stirring. The black crystalline solid was filtered and washed with alcohol and hot benzene. Yield: 0.22 g of complex VI, 90%.  $\chi_M = -262$  cm<sup>3</sup>/mol.

*Preparation of W<sub>3</sub>S<sub>4</sub>(aq)<sup>4+</sup>*

Complex VI (0.25 g) was treated with 5 ml of boiling concentrated HCl. The solution was filtered while hot and the blue solution was chromatographed on DOWEX-50WX2. The violet band was eluted with 0.2 M HCl. According to the elemental analysis data the W/S ratio was 3/3.98 ± 0.03. Yield: W<sub>3</sub>S<sub>4</sub>(aq)<sup>4+</sup>, 56%.

*Preparation of (Et<sub>4</sub>N)<sub>5</sub>W<sub>3</sub>S<sub>4</sub>(NCS)<sub>9</sub> (VII) and Cs<sub>5</sub>W<sub>3</sub>S<sub>4</sub>(NCS)<sub>9</sub> (VIII)*

Complex I (8.00 g) was heated in 40 g of a KNCS melt at 200–220 °C under stirring for 30 min. The cold melt was treated with 2 × 50 ml of water and the resulting green solution was added dropwise to a solution of Et<sub>4</sub>NBr (25 g) in water (50 ml). The precipitated green solid was filtered and washed with water, alcohol and ether. The material was recrystallized by diffusing ether vapours into a CH<sub>3</sub>CN solution of the complex. Yield: 12.12 g of complex VII, 89%.

Addition of CsCl to an aqueous solution of W<sub>3</sub>S<sub>4</sub>(NCS)<sub>9</sub><sup>5-</sup> at -5 °C leads to the crystallization of complex VIII in a 56% yield.

*Crystal structure determination*

The crystal structures were determined by X-ray diffraction analysis. The experiments were performed on an automated 'Hilger-Watts' diffractometer at 20 °C, Mo K $\alpha$  radiation, graphite monochromator. A  $\theta/2\theta$  scan technique was used,  $2\theta \leq 60^\circ$ . The corrections for absorption were made with the DIFABS program [19]. The structures were solved by direct methods and refined by block-diagonal least-squares methods using the anisotropic approximation for all non-hydrogen atoms. The calculations were per-

formed on the Eclipse S/200 computer with INEXTL programs [20].

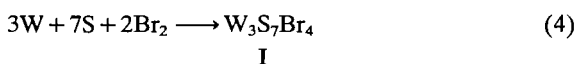
The single crystals of III were obtained by diffusing benzene vapours into an acetonitrile solution of the complex. The crystals of III, C<sub>48</sub>H<sub>40</sub>Br<sub>6</sub>W<sub>3</sub>P<sub>2</sub>S<sub>7</sub>, are orthorhombic,  $a = 18.082(2)$ ,  $b = 25.834(3)$ ,  $c = 27.370(2)$  Å,  $Z = 8$ , space group *Pbca*, 4758 independent reflections with  $I > 2\sigma(I)$ . The hydrogen atoms of III are placed into calculated positions with a fixed  $B_{iso} = 7$  Å<sup>2</sup> and were not refined. The final  $R$  was 0.049 ( $R_w = 0.055$ ). The coordinates of the non-hydrogen atoms of III are given in Table 2.

Single crystals of VI were selected from the reaction mixture. The crystals of VI are trigonal,  $a = 12.508(1)$ ,  $c = 10.112(1)$  Å,  $V = 1370.0$  Å<sup>3</sup>, space group *P31c*,  $Z = 2$ , 1174 independent reflections. A total of 1101 observed reflections with  $I > 2\sigma$  was used in the calculation. The cationic fragment of four light atoms in a special position on axis 3 has been revealed in a difference synthesis and included into the refinement with anisotropic thermal parameters. The H atoms have not been revealed. In the final result,  $R = 0.029$ ,  $R_w = 0.033$  from 1021 reflections with  $I > 4\sigma$ . The coordinates of the atoms of VI are given in Table 3.

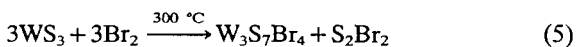
**Results and discussion**

*Preparation of W<sub>3</sub>S<sub>7</sub>Br<sub>4</sub> (I) and W<sub>3</sub>S<sub>7</sub>Cl<sub>4</sub> (II)*

The synthesis in ampoules from elements has been used to obtain a series of cluster chalcogenides of molybdenum and niobium [3, 21–23]. These methods allow the preparation of pure compounds including isotope-containing ones. In the case of tungsten, reaction (4) at 425 °C produced W<sub>3</sub>S<sub>7</sub>Br<sub>4</sub> [10], with a structure analogous to that of Mo<sub>3</sub>S<sub>7</sub>Cl<sub>4</sub> [24].



We prepared W<sub>3</sub>S<sub>7</sub>Br<sub>4</sub> from elements at 300 °C. It should be noted that the large energy of the W crystal lattice determines its low reactivity, and obtaining samples containing no metal tungsten requires a prolonged heating of 70 to 100 h. The degree of crystallinity of the resulting product is not high. Complex I of a poor crystallinity is also produced in a high yield by reaction (5)



Attempts to obtain single-phase W<sub>3</sub>S<sub>7</sub>Cl<sub>4</sub> samples proceeding from W and S<sub>2</sub>Cl<sub>2</sub> were not successful. Tungsten thiochloride (II) containing a small amount (about 5%) of unidentified phases has been obtained

TABLE 2. Atomic coordinates ( $\times 10^3$  for C and  $\times 10^4$  for remaining atoms) and  $B_{\text{iso}}$  for III

Atom	x	y	z	$B_{\text{iso}}$
W(1)	271(1)	4075(1)	555(1)	2.38(2)
W(2)	-993(1)	4094(1)	1106(1)	2.50(2)
W(3)	-939(1)	3522(1)	262(1)	2.53(3)
Br(11)	1498(2)	3649(1)	823(1)	4.16(9)
Br(12)	1231(1)	4752(1)	172(1)	3.23(8)
Br(21)	-1055(2)	3705(1)	1977(1)	4.67(9)
Br(22)	-1912(2)	4773(1)	1506(1)	4.52(9)
Br(31)	-1003(2)	2524(1)	256(1)	4.38(8)
Br(32)	-1698(2)	3419(1)	-560(1)	4.29(9)
S(1)	-395(4)	4842(2)	784(2)	3.2(2)
S(2)	171(4)	4538(3)	1355(2)	3.4(2)
S(3)	-1814(4)	4193(2)	432(2)	3.1(2)
S(4)	-2032(4)	3545(2)	818(2)	3.4(2)
S(5)	-331(4)	4164(2)	-218(2)	2.7(2)
S(6)	268(4)	3504(2)	-173(2)	3.3(2)
S(7)	-237(4)	3365(2)	975(2)	3.2(2)
P(1)	553(4)	2643(3)	3454(2)	3.4(2)
P(2)	698(5)	6199(3)	3490(3)	4.2(2)
C(1)	101(2)	267(1)	401(1)	3.6(8)
C(2)	154(2)	235(1)	416(1)	6(1)
C(3)	190(2)	236(1)	459(1)	8(1)
C(4)	177(2)	270(1)	489(1)	8(1)
C(5)	123(2)	302(2)	481(1)	11(2)
C(6)	85(2)	304(1)	434(1)	7(1)
C(7)	-34(2)	288(1)	352(1)	3.4(8)
C(8)	-70(2)	322(1)	317(1)	7(1)
C(9)	-145(2)	337(1)	323(1)	8(1)
C(10)	-183(2)	324(1)	363(1)	7(1)
C(11)	-152(2)	291(1)	397(1)	5.3(9)
C(12)	-80(2)	273(1)	391(1)	5.3(9)
C(13)	58(1)	198(1)	330(1)	3.4(8)
C(14)	115(2)	177(1)	304(1)	7(1)
C(15)	125(2)	117(1)	298(1)	8(1)
C(16)	72(2)	92(1)	321(1)	9(1)
C(17)	14(2)	108(1)	345(1)	8(1)
C(18)	6(2)	164(1)	349(1)	6(1)
C(19)	104(1)	299(1)	300(1)	3.3(7)
C(20)	159(2)	335(1)	310(1)	4.2(9)
C(21)	193(2)	366(1)	274(1)	5.4(9)
C(22)	169(2)	364(1)	226(1)	5.2(9)
C(23)	116(2)	328(1)	215(1)	7(1)
C(24)	81(2)	296(1)	251(1)	5.3(9)
C(25)	126(2)	670(2)	311(1)	9(1)
C(26)	156(3)	717(1)	326(2)	14(2)
C(27)	194(2)	746(1)	297(2)	11(2)
C(28)	199(3)	732(1)	249(2)	16(2)
C(29)	179(2)	697(2)	228(1)	13(2)
C(30)	136(2)	651(2)	259(2)	12(2)
C(31)	122(2)	614(1)	407(1)	5(1)
C(32)	198(2)	605(1)	404(1)	8(1)
C(33)	242(2)	596(1)	443(1)	10(1)
C(34)	206(3)	602(1)	486(1)	11(2)
C(35)	125(2)	612(1)	492(1)	8(1)
C(36)	81(2)	618(1)	449(1)	6(1)
C(37)	-20(2)	649(1)	360(1)	4.4(9)
C(38)	-27(2)	705(1)	365(1)	6(1)
C(39)	-97(2)	723(1)	374(1)	6(1)

(continued)

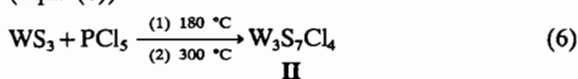
TABLE 2. (continued)

Atom	x	y	z	$B_{\text{iso}}$
C(40)	-157(2)	692(1)	377(1)	6(1)
C(41)	-160(2)	640(1)	372(1)	9(1)
C(42)	-90(3)	617(1)	364(1)	10(1)
C(43)	63(2)	555(1)	324(1)	4.2(9)
C(44)	105(3)	517(1)	343(1)	9(1)
C(45)	95(2)	470(1)	324(1)	12(2)
C(46)	48(2)	459(1)	284(1)	10(2)
C(47)	6(2)	496(1)	269(1)	8(1)
C(48)	13(2)	547(1)	286(1)	7(1)

TABLE 3. Atomic coordinates ( $\times 10^5$  for W and  $\times 10^4$  for remaining atoms) and equivalent isotropic thermal parameters  $B_{\text{eq}}$  for VI

Atom	x	y	z	$B_{\text{eq}}$
W	-52479(5)	-29997(5)	-25498(0)	1.29(2)
S(1)	-3766(4)	-1485(4)	-4179(4)	2.2(1)
S(2)	-1975(4)	-1085(4)	-3691(4)	2.6(1)
S(3)	-1983(4)	-998(4)	-1681(4)	2.7(1)
S(4)	-3434(4)	-2731(4)	-1233(4)	2.4(1)
S(5)	-5278(3)	-1549(4)	-1172(4)	1.8(1)
S(6)	-6667	-3333	-4285(5)	1.52(9)
X(1)	-5772(12)	-505(11)	-3719(13)	2.4(4)
X(2)	-6667	-3333	-7887(27)	6.7(7)
X(3)	-3674(22)	-1544(17)	-7799(22)	7.9(9)

at 300 °C from the product of the interaction, at 180 °C, of the equimolar quantities of  $\text{WS}_3$  and  $\text{PCl}_5$  (eqn. (6))



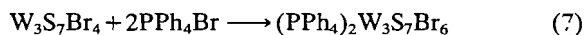
According to the X-ray structural data for  $\text{W}_3\text{S}_7\text{Br}_4$  [10] the  $\text{W}_3\text{S}_7^{4+}$  cluster fragments are linked to polymeric zigzag chain via halogen bridging atoms:  $\text{W}_3\text{S}_7\text{Br}_2\text{Br}_{4/2}$ . The thiochloride complex **II** appears to have an analogous structure. Such a polymeric structure of the compounds determines their chemical behaviour: both **I** and **II** are insoluble in organic solvents and non-volatile. In order for the polymeric  $\text{W}_3\text{S}_7\text{X}_4$  complexes to be the starting materials in the chemistry of triangular thiocomplexes of tungsten it is necessary to find reagents which are capable, in the interaction with them, of destroying the polymeric structure while preserving the cluster fragments. It has been shown by us earlier that the polymeric  $\text{Mo}_3\text{S}_7\text{X}_4$  in a  $\text{PPh}_4\text{X}$  melt could be converted to the salts  $(\text{PPh}_4)_2\text{Mo}_3\text{S}_7\text{X}_6$  ( $\text{X} = \text{Cl}, \text{Br}$ ) [6]. The structure of  $(\text{PPh}_4)_2\text{Mo}_3\text{S}_7\text{Cl}_6$  has been established by X-ray structural analysis [25]. The polymeric  $\text{NbS}_2\text{Cl}_2$  in a  $\text{KNCS}$  melt gives  $\text{K}_4\text{Nb}_2\text{S}_4(\text{NCS})_8$  [26]. The interaction of  $\text{Mo}_3\text{S}_7\text{X}_4$  with an aqueous

solution of  $(\text{NH}_4)_2\text{S}_x$  provides a convenient route to  $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13} \cdot 2\text{H}_2\text{O}$  [7, 8].

In the present work we have studied the interaction of the same reagents  $\text{PPh}_4\text{Br}$ ,  $\text{KNCS}$  and  $(\text{NH}_4)_2\text{S}_x$  with  $\text{W}_3\text{S}_7\text{Br}_4$  and obtained a series of triangular  $\text{W}_3\text{S}_7^{4+}$  and  $\text{W}_3\text{S}_7^{4+}$  complexes.

#### Preparation of $\text{W}_3\text{S}_7\text{X}_6^{2-}$ ( $\text{X}=\text{Cl}, \text{Br}$ ) salts

We have found that **I** interacts with  $\text{PPh}_4\text{Br}$  in a melt (eqn. (7))



This method is, however, not universal and cannot be used for obtaining salts with other organic cations, since the latter either have low melting points or decompose upon heating. To obtain  $\text{Et}_4\text{N}^+$  salts of  $\text{W}_3\text{S}_7\text{Br}_6^{2-}$  (and equally of  $\text{W}_3\text{S}_7\text{Cl}_6^{2-}$  and  $\text{Mo}_3\text{S}_7\text{X}_6^{2-}$ ) it is necessary to boil the starting polymers  $\text{M}_3\text{S}_7\text{X}_4$  ( $\text{M}=\text{Mo}, \text{W}; \text{X}=\text{Cl}, \text{Br}$ ) in concentrated  $\text{HX}$  acids in the presence of  $\text{Et}_4\text{NX}$ . The yields of these reactions are, as a rule, not high, not exceeding 40% and amounting sometimes only to several percent. We have not succeeded in finding a correlation between the history of the polymeric  $\text{M}_3\text{S}_7\text{X}_4$  (temperature, procedure and time of the synthesis) and their reactivity. It can be expected that the more is the degree of crystallinity and polymerization of  $\text{M}_3\text{S}_7\text{X}_4$  the less reactive is the compound. The salts **III–V** are air-stable and soluble in a series of organic solvents ( $\text{CH}_3\text{CN}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{DMF}$ ) which enables their chemical properties to be easily studied.

#### Structure of $(\text{Ph}_4\text{P})_2\text{W}_3\text{S}_7\text{Br}_6$ (**III**)

Figure 1 shows the structure of the  $\text{W}_3\text{S}_7\text{Br}_6^{2-}$  anion of **III**. The bond lengths and the valence angles of this anion are shown in Table 4. It has been proved by means of X-ray structural analysis that anion **III** is isostructural with the  $\text{W}_3\text{S}_7\text{Br}_6$  fragment

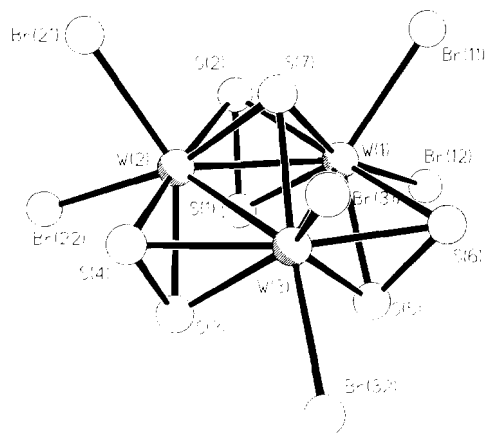


Fig. 1. Structure of the  $\text{W}_3\text{S}_7\text{Br}_6^{2-}$  anion.

of the chain polymer **I** [10]. The anion  $\text{W}_3\text{S}_7\text{Br}_6^{2-}$  contains 48 cluster valence electrons and conforms to the EAN rule. The average W–W distance is 2.739(2) Å. The complex is diamagnetic, suggesting the formation of single W–W bonds in the  $\text{W}_3$  triangle. There are two types of bromine atoms. For bromines lying on the same side of the  $\text{W}_3$  triangle as the  $\mu_3$ -S ligand (Br(11), Br(21), Br(31)), the average W–Br distance is 2.583(3) Å which is somewhat smaller than the W–Br bond length for the rest of the bromines, 2.661(3) Å. This can be explained by sterical factors associated with the  $\mu_2$ -S<sub>2</sub> effect. These ligands are inclined to the  $\text{W}_3$  plane so that the S(2), S(4) and S(6) atoms are practically in this plane (Table 5). No substantial non-valence interactions were found in the structure of **III**.

#### Vibrational spectra of $\text{W}_3\text{S}_7\text{Br}_6^{2-}$

Figure 2 shows vibrational spectra of  $(\text{Et}_4\text{N})_2\text{W}_3\text{S}_7\text{Br}_6$ .  $(\text{Et}_4\text{N})_2\text{W}_3^{34}\text{S}_7\text{Br}_6$  was obtained using the above procedures and its IR and Raman spectra were studied. For  $\text{W}_3\text{S}_7\text{Br}_6^{2-}$  a calculation of the normal vibrations has been performed using the following vibrations:  $\Gamma=10\text{A}_1(\text{IR}, \text{Raman}) + 4\text{A}_2 + 14\text{E}(\text{IR}, \text{Raman})$ . The experimental basis for the calculations was formed by: (i) vibrational frequencies in IR and Raman spectra; (ii) isotope shifts on going from  $\text{W}_3^{32}\text{S}_7\text{Br}_6^{2-}$  to  $\text{W}_3^{34}\text{S}_7\text{Br}_6^{2-}$ ; (iii) a comparison between the vibrational spectra of  $\text{M}_3\text{S}_7\text{X}_6^{2-}$  ( $\text{M}=\text{Mo}, \text{W}; \text{X}=\text{Cl}, \text{Br}$ ).

Table 6 lists the force constants; Table 7 summarizes the experimental and calculated frequencies of the normal vibrations for  $\text{W}_3\text{S}_7\text{Br}_6^{2-}$  and the shifts in these frequencies upon isotope exchange. Table 8 shows the distribution of the potential energy among the groups of equivalent vibrational coordinates. The results for  $\text{W}_3\text{S}_7\text{Br}_6^{2-}$  are in good agreement with the results of an earlier calculation of the normal vibrations for  $\text{Mo}_3\text{S}_7\text{Cl}_6^{2-}$  [17],  $\text{Mo}_3\text{S}_4\text{Se}_3\text{Cl}_6^{2-}$  [28] and  $\text{Mo}_3\text{S}_7(\text{S}_2)_3^{2-}$  [8]. The frequencies 558 and 552  $\text{cm}^{-1}$  are due to the S–S valence vibrations of the  $\mu_2$ -S<sub>2</sub> ligands. The 449  $\text{cm}^{-1}$  frequency is one of the most characteristic and results from the vibrations involving  $\mu_3$ -S.

#### Interaction of **I** with $(\text{NH}_4)_2\text{S}_x$ . Chemical properties of complex **VI**

The interaction of  $\text{W}_3\text{S}_7\text{Br}_4$  with  $(\text{NH}_4)_2\text{S}_x$  leads to conversion of  $\text{W}_3\text{S}_7^{4+}$  to  $\text{W}_3\text{S}_4^{4+}$  and formation of the complex  $\text{W}_3\text{S}_4(\text{S}_4)_3(\text{NH}_3)_3^{2-}$  (**VI**) whose structure has been determined by X-ray structural analysis. This result indicates a high lability of the equatorial sulfurs of the asymmetrically coordinated  $\mu_2$ -S<sub>2</sub> ligand. Although the formal result of the interaction of  $\text{Mo}_3\text{S}_7\text{Cl}_4$  and  $\text{Mo}_3\text{S}_7\text{Br}_4$  with  $(\text{NH}_4)_2\text{S}_x$  is the

TABLE 4. Bond lengths and angles in  $W_3S_7Br_6^{2-}$ 

Bond lengths (Å)			
W(1)—W(2)	2.738(1)	W(2)—S(3)	2.384(6)
W(1)—W(3)	2.735(2)	W(2)—S(4)	2.484(7)
W(1)—Br(11)	2.582(3)	W(2)—S(7)	2.355(7)
W(1)—Br(12)	2.680(3)	W(3)—Br(31)	2.585(3)
W(1)—S(1)	2.406(7)	W(3)—Br(32)	2.649(3)
W(1)—S(2)	2.503(6)	W(3)—S(3)	2.395(7)
W(1)—S(5)	2.393(6)	W(3)—S(4)	2.495(7)
W(1)—S(6)	2.480(6)	W(3)—S(5)	2.388(6)
W(1)—S(7)	2.352(6)	W(3)—S(6)	2.487(7)
W(2)—W(3)	2.744(1)	W(3)—S(7)	2.363(6)
W(2)—Br(21)	2.589(3)	S(1)—S(2)	2.027(9)
W(2)—Br(22)	2.655(3)	S(3)—S(4)	2.021(9)
W(2)—S(1)	2.386(7)	S(5)—S(6)	2.027(9)
W(2)—S(2)	2.492(7)		
Bond angles (°)			
W(2)W(1)W(3)	60.19(4)	S(1)W(2)S(7)	109.3(2)
W(2)W(1)Br(11)	124.63(8)	S(2)W(2)S(3)	133.5(2)
W(2)W(1)Br(12)	138.07(7)	S(2)W(2)S(4)	171.6(2)
W(2)W(1)S(1)	54.8(2)	S(2)W(2)S(7)	85.5(2)
W(2)W(1)S(2)	56.6(2)	S(3)W(2)S(4)	49.0(2)
W(2)W(1)S(5)	96.0(2)	S(3)W(2)S(7)	109.3(2)
W(2)W(1)S(6)	116.8(2)	S(4)W(2)S(7)	86.2(2)
W(2)W(1)S(7)	54.5(2)	W(1)W(3)W(2)	59.97(4)
W(3)W(1)Br(11)	123.22(8)	W(1)W(3)Br(31)	124.09(8)
W(3)W(1)Br(12)	138.19(7)	W(1)W(3)Br(32)	135.76(8)
W(3)W(1)S(1)	96.2(2)	W(1)W(3)S(3)	95.3(2)
W(3)W(1)S(2)	116.7(2)	W(1)W(3)S(4)	116.3(2)
W(3)W(1)S(5)	55.0(1)	W(1)W(3)S(5)	55.2(1)
W(3)W(1)S(6)	56.7(2)	W(1)W(3)S(6)	56.5(2)
W(3)W(1)S(7)	54.7(2)	W(1)W(3)S(7)	54.4(2)
Br(11)W(1)Br(12)	80.43(9)	W(2)W(3)Br(31)	122.87(8)
Br(11)W(1)S(1)	135.1(2)	W(2)W(3)Br(32)	138.64(8)
Br(11)W(1)S(2)	91.0(2)	W(2)W(3)S(3)	54.8(2)
Br(11)W(1)S(5)	133.1(2)	W(2)W(3)S(4)	56.4(2)
Br(11)W(1)S(6)	88.7(2)	W(2)W(3)S(5)	96.0(2)
Br(11)W(1)S(7)	82.2(2)	W(2)W(3)S(6)	116.3(2)
Br(12)W(1)S(1)	83.5(2)	W(2)W(3)S(7)	54.3(2)
Br(12)W(1)S(2)	94.4(2)	Br(31)W(3)Br(32)	82.56(9)
Br(12)W(1)S(5)	83.4(2)	Br(31)W(3)S(3)	134.1(2)
Br(12)W(1)S(6)	94.4(2)	Br(31)W(3)S(4)	89.6(2)
Br(12)W(1)S(7)	162.6(2)	Br(31)W(3)S(5)	135.4(2)
S(1)W(1)S(2)	48.7(2)	Br(31)W(3)S(6)	91.0(2)
S(1)W(1)S(5)	85.5(2)	Br(31)W(3)S(7)	81.9(2)
S(1)W(1)S(6)	134.4(2)	Br(32)W(3)S(3)	84.0(2)
S(1)W(1)S(7)	108.7(2)	Br(32)W(3)S(4)	96.3(2)
S(2)W(1)S(5)	134.0(2)	Br(32)W(3)S(5)	80.8(2)
S(2)W(1)S(6)	171.1(2)	Br(32)W(3)S(6)	92.6(2)
S(2)W(1)S(7)	85.3(2)	Br(32)W(3)S(7)	164.3(2)
S(5)W(1)S(6)	49.1(2)	S(3)W(3)S(4)	48.8(2)
S(5)W(1)S(7)	109.3(2)	S(3)W(3)S(5)	84.6(2)
S(6)W(1)S(7)	85.9(2)	S(3)W(3)S(6)	133.3(2)
W(1)W(2)W(3)	59.84(4)	S(3)W(3)S(7)	108.6(2)
W(1)W(2)Br(21)	122.41(8)	S(4)W(3)S(5)	133.1(2)
W(1)W(2)Br(22)	139.59(8)	S(4)W(3)S(6)	171.1(2)
W(1)W(2)S(1)	55.5(2)	S(4)W(3)S(7)	85.8(2)
W(1)W(2)S(2)	56.9(2)	S(5)W(3)S(6)	49.1(2)
W(1)W(2)S(3)	95.5(2)	S(5)W(3)S(7)	109.1(2)
W(1)W(2)S(4)	116.5(2)	S(6)W(3)S(7)	85.5(2)

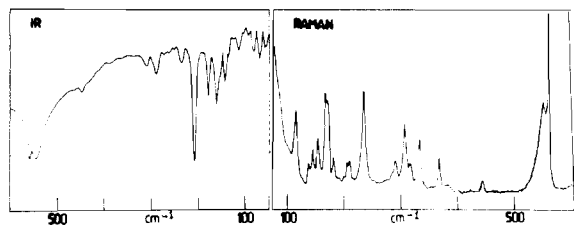
(continued)

TABLE 4. (continued)

Bond angles (°)			
W(1)W(2)S(7)	54.4(2)	W(1)S(1)W(2)	69.7(2)
W(3)W(2)Br(21)	124.50(8)	W(1)S(1)S(2)	68.1(3)
W(3)W(2)Br(22)	136.54(8)	W(2)S(1)S(2)	68.2(3)
W(3)W(2)S(1)	96.4(2)	W(1)S(2)W(2)	66.5(2)
W(3)W(2)S(2)	116.7(2)	W(1)S(2)S(1)	63.2(3)
W(3)W(2)S(3)	55.2(2)	W(2)S(2)S(1)	62.7(3)
W(3)W(2)S(4)	56.7(2)	W(2)S(3)W(3)	70.1(2)
W(3)W(2)S(7)	54.6(2)	W(2)S(3)S(4)	68.1(3)
Br(21)W(2)Br(22)	81.41(9)	W(3)S(3)S(4)	68.2(3)
Br(21)W(2)S(1)	132.4(2)	W(2)S(4)W(3)	66.9(2)
Br(21)W(2)S(2)	87.9(2)	W(2)S(4)S(3)	62.9(3)
Br(21)W(2)S(3)	136.7(2)	W(3)S(4)S(3)	63.0(3)
Br(21)W(2)S(4)	92.1(2)	W(1)S(5)W(3)	69.8(2)
Br(21)W(2)S(7)	81.6(2)	W(1)S(5)S(6)	67.7(3)
Br(22)W(2)S(1)	84.2(2)	W(3)S(5)S(6)	68.0(3)
Br(22)W(2)S(2)	96.3(2)	W(1)S(6)W(3)	66.8(2)
Br(22)W(2)S(3)	81.8(2)	W(1)S(6)S(5)	63.2(2)
Br(22)W(2)S(4)	92.0(2)	W(3)S(6)S(5)	62.9(2)
Br(22)W(2)S(7)	162.8(2)	W(1)S(7)W(2)	71.1(2)
S(1)W(2)S(2)	49.0(2)	W(1)S(7)W(3)	70.9(2)
S(1)W(2)S(3)	84.8(2)	W(2)S(7)W(3)	71.1(2)
S(1)W(2)S(4)	133.6(2)		

TABLE 5. Deviation of the  $W_3S_7Br_6^{2-}$  atoms from the plane of the three W atoms

Atom	Deviation (Å)
Br(11)	-1.972(3)
Br(12)	1.365(3)
Br(21)	-1.996(3)
Br(22)	1.361(3)
Br(31)	-1.993(3)
Br(32)	1.406(3)
S(1)	1.636(6)
S(2)	-0.131(7)
S(3)	1.646(6)
S(4)	-0.099(6)
S(5)	1.639(6)
S(6)	-0.127(6)
S(7)	-1.748(6)

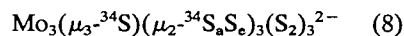
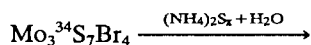
Fig. 2. IR and Raman spectra of  $(Et_4N)_2W_3S_7Br_6$ .

replacement of the halogenide ligands by disulfide ones to form  $Mo_3S_{13}^{2-}$  [7], an analysis of these reactions by vibrational spectroscopy using  $^{34}S$  isotope

TABLE 6. Force constants in  $W_3(\mu_3-S)(\mu_2-S_2)_3Br_6^{2-}$ 

Bond	Force constant (mdyn/Å)
W-W	1.2
W- $\mu_3$ -S(7)	2.0
W- $\mu_2$ -S(2)	1.5
W- $\mu_2$ -S(1)	1.8
W-Br(11)	1.3
W-Br(12)	1.4
S(1)-S(2)	2.4

has shown that the exchange involves also the sulfurs of the  $\mu_2$ - $S_2$  ligand, with only the  $Mo_3S_4^{4+}$  core remaining intact [8] (eqn. (8))



Complex VI represents a black crystalline substance moderately soluble in water and polar solvents from which it cannot, however, be isolated without decomposition.

We have shown earlier [17] that the interaction of  $Mo_3S_{13}^{2-}$  with HX (X = Cl, Br, I) can provide a convenient method for obtaining thiohalide complexes  $Mo_3S_7X_6^{2-}$ . Interacting HCl with VI produces a blue solution which can be purified chromatographically. The UV spectrum of the eluate indicates the presence of  $W_3S_4^{4+}$  chromophore and is in a good agreement with that given by Shibahara



TABLE 7. Experimental ( $\text{Et}_4\text{N}^+$  salt) and calculated vibrational frequencies of  $\text{W}_3\text{S}_7\text{Br}_6^{2-}$  and their shifts upon isotope exchange

$\nu_{\text{exp}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{calc}}$ ( $\text{cm}^{-1}$ )	$\Delta\nu$ for $\text{W}_3^{32}\text{S}_7\text{Br}_6^{2-}$ and $\text{W}_3^{34}\text{S}_7\text{Br}_6^{2-}$	
		Exp.	Calc.
180, Raman	182	0	0.5
210, Raman, IR	209	2	1.5
	223		6.4
	230		6.2
235, Raman, IR	235	0	1.0
	289		6.7
	294	9	8.2
293, Raman, IR	302		5.2
	309	7	6.7
320, Raman, IR	319	7	6.2
335, Raman	337	8	8.7
372, Raman	370	8	8.8
449, Raman, IR	449	11	12.0
550, Raman	552	16	16.0
560, Raman, IR	558	17	16.3

TABLE 8. Distribution of the potential energy (%) among the groups of equivalent vibrational coordinates

Bands ( $\text{cm}^{-1}$ )	W-W	W- $\mu_3$ -S(7)	W- $\mu_2$ -S(1)	W- $\mu_2$ -S(2)	W-Br(11)	W-Br(12)	S-S
119, $A_1$	67	0	0	4	11	18	0
182, $A_1$	0	3	4	2	61	30	0
209, E	3	2	7	7	27	54	0
223, $A_2$	0	0	65	35	0	0	0
230, E	1	5	80	8	1	4	1
235, $A_1$	22	0	0	9	17	52	0
289, E	1	14	9	70	4	2	0
294, $A_1$	1	1	75	3	2	0	18
302, $A_2$	0	0	44	56	0	0	0
309, E	1	75	7	11	1	5	0
319, E	3	0	68	10	0	0	19
337, E	0	1	13	80	2	0	4
370, $A_1$	2	2	14	72	2	0	7
449, $A_1$	1	97	0	0	0	1	0
552, E	0	0	12	11	0	0	77
558, $A_1$	0	0	11	14	0	0	75

*et al.* for  $\text{W}_3\text{S}_4(\text{H}_2\text{O})_9^{4+}$  [11]. Our attempts to isolate from these solutions thiohalogenide complexes  $\text{W}_3\text{S}_4\text{X}_9^{5-}$  with different cations ( $\text{Cs}^+$ ,  $\text{bpyH}^+$ ,  $\text{EtCOONH}_3^+$ ,  $\text{Et}_4\text{N}^+$ ) were not successful. The splitting off of the  $\text{S}_4^{2-}$  ligands also occurs in  $\text{HBr}$  medium,  $\text{HF}/\text{NH}_4\text{F}$  and in cold concentrated  $\text{H}_2\text{SO}_4$ . However, the reaction is not of a general character, VI is stable towards  $\text{CH}_3\text{COOH}$ ,  $\text{CF}_3\text{COOH}$  and  $\text{H}_3\text{PO}_4$ .

The thermal decomposition of VI under vacuum at  $380^\circ\text{C}$  has produced X-ray amorphous  $\text{WS}_2$  with a rather high specific surface area ( $44\text{ m}^2/\text{g}$ ).

#### Interaction of $\text{W}_3\text{S}_7\text{Br}_4$ with KNCS

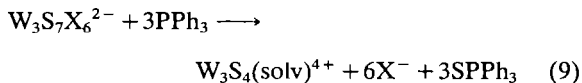
$\text{W}_3\text{S}_7\text{Br}_4$  quickly dissolves in a KNCS melt giving it a green colour. Treatment of the melt with water

and  $\text{Et}_4\text{NBr}$  or  $\text{CsCl}$  results in formation of the corresponding  $\text{Q}_5\text{W}_3\text{S}_4(\text{NCS})_9$  salts (VII, VIII). In the extraction of the melt with benzene sulfur was isolated. Shibahara *et al.* described the synthesis of  $\text{W}_3\text{S}_4(\text{H}_2\text{O})_9^{4+}$  by the reduction of  $(\text{NH}_4)_2\text{WS}_4$  in  $\text{HCl}$  from which the  $(\text{bpyH})_5\text{W}_3\text{S}_4(\text{NCS})_9 \cdot 3\text{H}_2\text{O}$  salt in a 17% yield has been obtained and structurally characterized [11].

Under the action of nucleophiles, such as  $\text{CN}^-$ , phosphines, or an 'internal nucleophile'—the terminal  $\text{S}_2$  ligand, the  $\text{Mo}_3\text{S}_7^{4+}$  clusters can produce  $\text{Mo}_3\text{S}_4^{4+}$  [29].

It has also been found that the  $\text{W}_3\text{S}_7\text{X}_6^{2-}$  salts interact with  $\text{PPh}_3$  in a  $\text{CH}_3\text{CN}$  solution to form

blue solutions which showed an electronic spectrum characteristic of a  $W_3S_4^{4+}$  chromophor



Thus, convenient methods for the synthesis of  $W_3S_7^{4+}$  and  $W_3S_4^{4+}$  clusters both in aqueous and non-aqueous media have been found which makes possible a wide study of their chemical properties.

*Structure of  $(NH_4)(H)(H_2O)_3W_3S_{16}(NH_3)_3$  (VI)*

The triangular anionic cluster  $W_3(\mu_3-S)(\mu_2-S)_3(S_4)_3(NH_3)_3^{2-}$  presented in Fig. 3, occupies in the crystal a special position on axis 3 passing through  $\mu_3-S(6)$  and the center of the  $W_3$ -triangle perpendicular to its plane. The cationic fragment of VI occupies an analogous special position, i.e. the X(1) atom on axis 3 in a planar-trigonal environment of three X(2) atoms at a distance of 3.26(3) Å. The positions of all non-hydrogen atoms have been found objectively but the nature of the light atoms X(1), X(2) can only be suggested (see below).

The cluster fragment  $W_3(\mu_3-S)(\mu_2-S)_3^{4+}$  has a structure typical of Mo and W derivatives. The W-W distances of 2.784(1) Å in the triangular framework are close to the W-W distances of (bpyH)<sub>5</sub>-W<sub>3</sub>S<sub>4</sub>(NCS)<sub>9</sub>·3H<sub>2</sub>O [11], [W<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>(dmpe)<sub>3</sub>]PF<sub>6</sub>·

H<sub>2</sub>O, [W<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>(depe)<sub>3</sub>]PF<sub>6</sub> and [W<sub>3</sub>S<sub>4</sub>H<sub>3</sub>(dmpe)<sub>3</sub>]-BPh<sub>4</sub> [12, 14]. The W-S(6) (2.379(4) Å) and W-S(5) (2.32 Å (av.)) distances are close to the typical separations for the corresponding bonds in W<sub>3</sub>S<sub>4</sub><sup>4+</sup> derivatives which are 2.33–2.36 Å for W- $\mu_3$ -S and 2.28–2.31 Å for W- $\mu_2$ -S [11, 12, 14]. Geometrical parameters of the cluster compound VI are listed in Table 9.

The coordination number of the tungsten atoms in the anion with respect to the ligands (i.e. without the metal-metal bonds) is equal to 6. The nitrogen atoms of the NH<sub>3</sub> molecules lie opposite to the  $\mu_2$ -S ligands. A refinement of the preliminary structural data [18] has led to close values of the W-S(1) and W-S(4) bonds occupying *cis* (2.496(4) Å) and *trans* (2.505(5) Å) positions, respectively, with respect to the  $\mu_3$ -S ligand. The average length of the terminal W-S bond is 2.50 Å. In the [(S<sub>4</sub>)W(S)( $\mu_2$ -S)<sub>2</sub>W(S)(S<sub>4</sub>)]<sup>2-</sup> cluster the separations between the tungsten and the sulfur of the tetrasulfide ligand are considerably smaller, 2.38–2.40 Å [30]. The reasons for the longer distances are not clear but it is probably this bond lengthening that is responsible for the easiness of the separation of the S<sub>4</sub><sup>2-</sup> ligands in VI under the action of HX. The conformation of the MS<sub>4</sub> metalocycles in VI correspond to a distorted envelope (see torsion angles in Table 9). The preliminary report of S-S bond alternation in VI [18] has been confirmed.

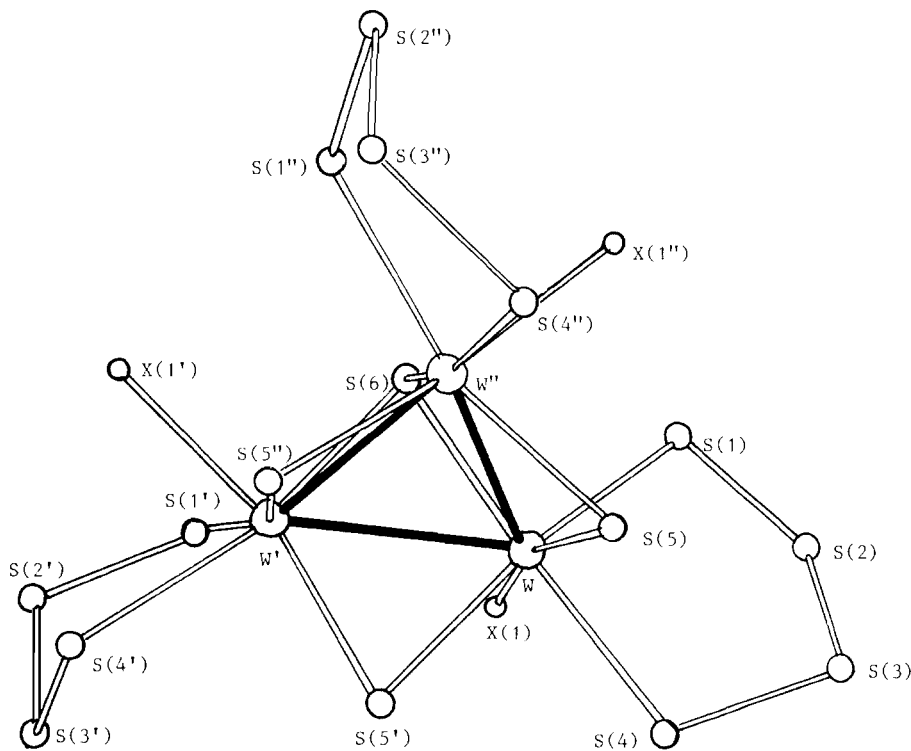


Fig. 3. Structure of the  $W_3S_{16}(NH_3)_3^{2-}$  anion.

TABLE 9. Bond lengths, bond angles and torsion angles in  $W_3S_{16}(NH_3)_3^{2-}$ 

Bond lengths (Å)			
W—W'	2.7836(9)	W—S(6)	2.379(4)
W—W''	2.7836(8)	W—X(1)	2.27(1)
W—S(1)	2.496(4)	S(1)—S(2)	2.096(7)
W—S(4)	2.505(5)	S(2)—S(3)	2.036(6)
W—S(5)'	2.303(4)	S(3)—S(4)	2.065(6)
W—S(5)	2.337(4)	X(2)—X(3)	3.26(3)
Bond angles (°)			
W'WS(1)	98.9(1)	S(4)WS(5)	81.3(1)
W'WS(4)	140.2(1)	S(4)WS(6)	164.1(1)
W'WS(5)'	53.7(1)	S(4)WX(1)	79.8(4)
W'WS(5)	98.7(1)	S(5)WS(5)'	98.6(1)
W'WS(6)	54.20(8)	S(5)WS(6)	106.2(1)
W'WX(1)	140.0(4)	S(5)WX(1)	165.8(4)
W''WS(1)	135.6(1)	S(5)'WS(6)	105.2(1)
W''WS(4)	133.9(1)	S(5)'WX(1)	84.1(4)
W''WS(5)'	99.5(1)	S(6)WX(1)	86.3(4)
W''WS(5)	52.6(1)	WS(1)S(2)	109.0(2)
W''WS(6)	54.20(8)	S(1)S(2)S(3)	102.4(3)
W''WX(1)	93.2(4)	S(2)S(3)S(4)	100.8(3)
S(1)WS(4)	88.3(1)	WS(4)S(3)	106.6(2)
S(1)WS(5)	95.7(1)	WS(5)W''	73.7(1)
S(1)WS(5)'	161.8(1)	WS(6)W'	71.59(9)
S(1)WS(6)	81.5(1)	WS(6)W''	71.59(9)
S(1)WX(1)	79.4(4)	X(3)X(2)X(3)	119.9(8)
S(4)WS(5)	86.7(1)	X(3)X(2)X(3)	119.9(8)
Torsion angles (°)			
S(4)WS(1)S(2)	8.0(3)	S(2)S(3)S(4)W	-53.3(2)
WS(1)S(2)S(3)	-39.8(2)	S(3)S(4)WS(1)	25.8(3)
S(1)S(2)S(3)S(4)	57.7(3)		

The presence of the cluster of three strongly absorbing W atoms made it difficult to identify the light atoms X(1)–X(2) in the cation and  $NH_3$  in the anion by a least-squares refinement or from the positions of the H atoms. A hypothetical composition  $[W_3S_{16}(H_2O)_3][(NH_4)_3HSO_3]$  is discussed in ref. 18. Further refinement allowed unambiguous location of the light atoms in the cationic part of VI, but their nature can only be suggested from the values of the interatomic distances.

The X(1)–X(2) (3.26(3) Å) distances considerably exceed the usual lengths of the OH...O bonds in hydrated oxonium cations (2.2–2.7 Å) and are somewhat longer than the N...O distance in systems with a NH...O hydrogen bond (2.8–2.9 Å) [31]. On the other hand, the weak hydrogen bond involving the ammonium cation varies over a wide range of interatomic distances. Thus in the structure of ammonium hydrate  $NH_3 \cdot 3H_2O$  the N...O distances are 3.21–3.29 Å [31] whereas in a series of complexes of the ammonium cation with crown ethers they are in the range 2.9–3.2 Å [32, 33]. Taking into account

the possibility of a disordering of the X(1) and X(2) atoms in the highly symmetrical structure of VI (as indirectly suggested by the high values of the thermal parameters of these atoms), the cationic part of VI can be tentatively interpreted as a hydrated ammonium ion  $[(NH_4)(H_2O)_3]^+$ .

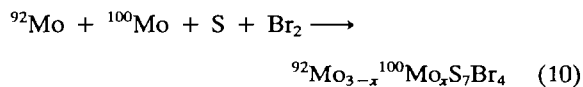
For re-formulating the ligand in  $W_3S_4(S_4)_3L_3^{2-}$  as  $NH_3$  and not as  $H_2O$  the following considerations were used: (i) analysis for nitrogen indicates a rather large content of the element; (ii) the 1228  $cm^{-1}$  band in the IR spectrum of VI can be attributed to the vibrations of coordinated ammonia [34]; (iii) the length of the terminal W–L bond 2.27 Å markedly increases as compared with the usual W–O lengths for the  $H_2O$  ligands in the trinuclear clusters, containing the  $\mu_3$ -O bridges  $W_3(\mu_3-O)_n(RCOO)_6(H_2O)_3^{2+}$  ( $n = 1, 2$ ) (2.09–2.18 Å) [35]. This is in agreement with the increased value for the nitrogen covalent radius as compared with oxygen. The W–N bond length in VI is in agreement with that in  $W(CPh)(CO)_2py_2Br_2$  (av. 2.27 Å) [36] and with Mo–N in the cubane-like cluster  $Mo_3FeS_4(NH_3)_9(H_2O)^{4+}$

(av. 2.27 Å) [15]. Considering the closeness of the metallic radii of Mo (1.40 Å) and W (1.41 Å), the anion VI can be thought to contain ammonia molecules as ligand L.

The proposed preliminary identification of the light atoms in the cation must lead to an odd number of electrons in the cluster. There are no S–H vibrations in the IR spectra of VI. To explain the diamagnetism it is necessary to assume either the presence of a hydride ligand in the anion with the trinuclear W<sub>3</sub> cluster or localization of an 'extra' proton on one of the X(2) atoms. Transformation of one aqua-ligand X(2)H<sub>2</sub> to the oxonium ion must then lead to actual distortions of the symmetrical structure of the cationic aggregate VI, i.e. to a disorder of the X(2) atoms in the highly symmetrical structure of VI. The above mentioned lengthening of the X(1)–X(2) distance compared with the usual H...O bond length can be considered as an indirect evidence for the latter assumption.

#### Attempt of the synthesis of heterometallic W<sub>3-x</sub>Mo<sub>x</sub>S<sub>7</sub>Br<sub>4</sub> clusters

With convenient synthesis methods of W<sub>3</sub>S<sub>7</sub>Br<sub>4</sub> and Mo<sub>3</sub>S<sub>7</sub>Br<sub>4</sub> from metals or MS<sub>3</sub> at hand, we have attempted to synthesize heterometallic thiobromide clusters containing Mo and W atoms in one triangle. The following synthetic result formed the basis for formulating such an experiment: the interaction of a mixture of <sup>92</sup>Mo and <sup>100</sup>Mo isotopes with sulfur was observed to afford a mixed-isotope triangular complex (eqn. (10))



This was concluded from a comparison of the vibrational spectra of a sample prepared by eqn. (10) and of samples which were certainly known to be <sup>92</sup>Mo<sub>3</sub>S<sub>7</sub>Br<sub>4</sub> and <sup>100</sup>Mo<sub>3</sub>S<sub>7</sub>Br<sub>4</sub> [16]. It appears, that the Mo<sub>3</sub>S<sub>7</sub>Br<sub>4</sub> synthesis from metallic Mo proceeds via mononuclear compounds.

A different result is produced in the interaction of a mixture of Mo and W with sulfur and bromine or of a mixture of MoS<sub>3</sub> and WS<sub>3</sub> with bromine at 300 °C. The vibrational spectra of the resulting products represent a superposition of the spectra of individual M<sub>3</sub>S<sub>7</sub>Br<sub>4</sub>. An additional evidence is provided by the results of the interaction of the products of these reactions with HBr/Et<sub>4</sub>NBr resulting in the crystallization of a mixture of (Et<sub>4</sub>N)<sub>2</sub>Mo<sub>3</sub>S<sub>7</sub>Br<sub>6</sub> and corresponding W salt in low yields. Melting together with KNCS produced only W<sub>3</sub>S<sub>4</sub>(NCS)<sub>9</sub><sup>5-</sup> salts. We could not obtain heterometallic triangular thio-complexes in all cases. This implies that under the reaction

conditions both metallic Mo and W, and a mixture of MoS<sub>3</sub> and WS<sub>3</sub> react independently.

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