Inorganica Chimica Acta, *163* (1989) 65–71

Synthesis and Characterization of Binuclear Thiohalide Complexes of Tungsten(V)

V. P. FEDIN*, YU. V. MIRONOV, M. N. SOKOLOV, YU. I. MIRONOV and V. E. FEDOROV

Institute of Inorganic Chemistry, Siberian Branch of the Academy of Sciences of the U.S.S.R., Prospekt Lavrentyeva 3, Novosibirsk 630090 (U.S.S.R.)

(Received December 3, 1988; revised March 29, 1989)

Abstract

Interaction of $(Et_4N)_2WS_4$ with HX (X = Cl, Br) in methylene chloride has been studied. Conditions have been found which lead to the formation of tetraethylammonium salts containing $W_4S_{12}^{2-}$, $W_3S_9^{2-}$, $W_2S_4X_4^{2-}$, $W_2S_3Br_8^{2-}$ and $W_2S_4X_8^{2-}$. Mutual transformations between binuclear thiohalide complexes of tungsten have been studied. Complex $W_2S_3Br_6\cdot 2CH_3CN$ has been obtained by interacting Br_2 with $(Et_4N)_2W_2S_4Br_4$ in acetonitrile. Boiling of $(Et_4N)_2W_2S_3Br_8$ with elemental sulfur in acetonitrile produced complex $(Et_4N)_2W_2S_4Br_8$ whose structure was established by X-ray structural analysis.

Introduction

Interaction of solutions of salts of the mononuclear tetrathiometallate ion WS_4^{2-} with acids [1] is one of the general methods of the synthesis of polynuclear thio- and oxothiocomplexes of tungsten. The reactions are carried out both in aqueous solutions and in organic solvents. HF, HCl, H_2SO_4, CH_3COOH and others are used as acids. Salts containing bi-, tri- and tetranuclear anions $W_2S_{11}^{2-}$ [2], $HW_2S_{11}^{-}$ [3], $W_3S_9^{2-}$ [4], $W_3S_8^{2-}$ [5], $W_3S_8O^{2-}$ [6], $W_4S_{12}^{2-}$ [7] have been obtained by this method.

The composition of the reaction products of the acidolysis of WS_4^{2-} depends on such factors as the nature of the acid, solvent and cation as well as on the concentration of the reactants and their ratio. In all of the reactions studied previously the anions of acids did not enter into the composition of the resulting thiotungstate complexes.

In the present work we have studied the interaction of $(Et_4N)_2WS_4$ with hydrogen chloride (Scheme 1) and hydrogen bromide (Scheme 2) in methylene chloride. The reaction produced tetraethylammonium salts of polynuclear thiocomplexes or tetraethylammonium salts of binuclear thiohalide complexes depending on the reaction conditions. First examples of the preparation of thiohalide complexes from thiocomplexes have been found.

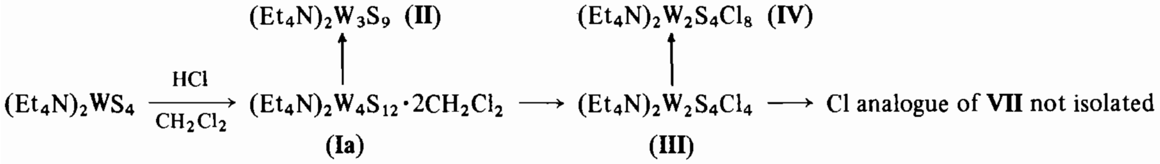
Experimental

Chemicals

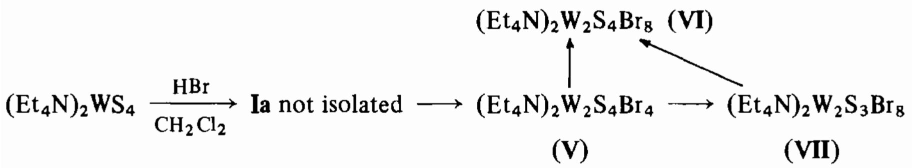
$(Et_4N)_2WS_4$ was obtained by the procedure described in ref. 8. Acetonitrile and methylene chloride were refluxed two times over P_4O_{10}.

Characterization Methods

IR spectra were measured in KBr on a IR-75 (Carl Zeiss) instrument in the 4000–400 cm^{-1} region and in polyethylene on a IFS-113 Fourier spectrometer (Bruker) in the 600–20 cm^{-1} region. Raman spectra



Scheme 1. Reaction with HCl.



Scheme 2. Reaction with HBr.

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

TABLE 1. Analytical and spectroscopic data for thiocomplexes of tungsten

Compound	Colour	Analyses			Vibrational spectra		
		Element	Found	Calculated	IR (cm^{-1})	Raman (cm^{-1})	Assignment
$(Et_4N)_2W_4S_{12}\cdot 2CH_2Cl_2$ (Ia)	red–violet	C	13.9	13.9	529s	537s	$\nu(W_c{=}S)$
		H	2.8	2.8	500vs	507vs	$\nu(W_t{=}S)$
		N	1.8	1.7	460s		$\delta(W_2S_2)$
		W	47.4	47.1	448m		
		S	25.0	24.8			
$(Et_4N)_2W_4S_{12}\cdot C_6H_6$ (Ib)	dark red	C	18.2	18.1			
		H	3.3	3.2			
		N	1.8	1.9			
		W	48.5	50.4			
		S	26.3	26.4			
$(Et_4N)_2W_4S_{12}$ (I)	dark violet	C	14.0	13.9			
		H	2.9	2.9			
		N	2.0	2.2			
		W	53.0	53.3			
		S	29.5	28.9			
$(Et_4N)_2W_3S_9$ (II)	dark red	C	17.5	17.5	527s	526s	$\nu(W_c{=}S)$
		H	3.9	3.7	499vs	507vs	$\nu(W_t{=}S)$
		N	2.5	2.5	464m	495m	$\delta(W_2S_2)$
		W	49.8	50.1	448m	459m	
		S	26.2	26.2			

were obtained for powders on a DFS-24 instrument using the 632.8 nm line of a He–Ne laser for excitation. Powder diffraction data were obtained on DRON-3M (Mo Kα radiation). Magnetic susceptibility was determined by the Faraday method. PMR spectra were recorded on a BS-567 (Tesla) instrument with TMS as internal standard. Tungsten and sulfur were determined by the weight method as WO_3 and $BaSO_4$, respectively; halogen, by potentiometric titration with a 0.05 M solution of $AgNO_3$. C, H and N were determined in the laboratory of Microanalysis of the Institute of Organic Chemistry (Novosibirsk). Analytical and spectroscopic data for thio- and thiohalide complexes are summarized in Tables 1 and 2.

Syntheses

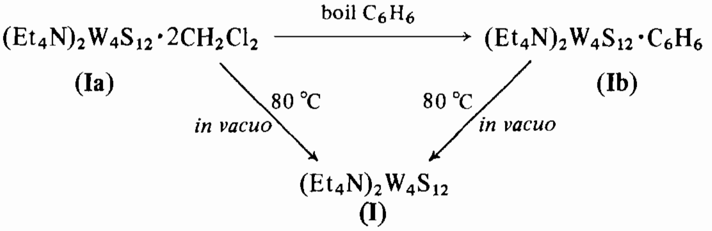
Preparation of $(Et_4N)_2W_4S_{12}\cdot 2CH_2Cl_2$ (Ia) and $(Et_4N)_2W_3S_9$ (II)

Dry hydrogen chloride was passed through a suspension of $(Et_4N)_2WS_4$ in CH_2Cl_2 (2.00 g in 150 ml) until the yellow precipitate of the starting complex disappeared (here and in other cases the flow rate of HX was approximately 100 ml/min). The newly formed crystals were immediately filtered off, washed with alcohol and ether, and vacuum dried. Yield: 0.95 g of **Ia**, 70%. After 4 h 0.15 g of complex **II**, 12%, was obtained from the mother solution at –5 °C.

Boiling of **Ia** in benzene produced the $(Et_4N)_2W_4S_{12}\cdot C_6H_6$ (**Ib**) solvate in quantitative yield. Heating of **Ia** or **Ib** under vacuum at 80 °C produced complex $(Et_4N)_2W_4S_{12}$ (**I**) in quantitative yield (Scheme 3).

Preparation of $(Et_4N)_2W_2S_4Cl_4$ (III) and $(Et_4N)_2W_2S_4Cl_8$ (IV)

HCl was passed through a suspension of $(Et_4N)_2WS_4$ in CH_2Cl_2 (2.00 g in 150 ml) until the yellow precipitate of the starting complex disappeared and for another 20 min until **Ia** dissolved. The reaction mixture was then kept for 24 h in a closed vessel. The



Scheme 3. Reactions of tetranuclear complexes.

TABLE 2. Analytical and spectroscopic data for thiohalide complexes of tungsten

Compound	Colour	Analyses			Vibrational spectra		
		Element	Found	Calculated	IR (cm^{-1})	Raman (cm^{-1})	Assignment
$(Et_4N)_2W_2S_4Cl_4$ (III)	green	C	21.0	21.3	527vs	534w	$\nu(W{=}S)$
		H	4.5	4.4	513w	524m	
		N	3.4	3.1	458vs	455m	$\delta(W_2S_2)$
		W	40.9	40.9	310s		$\nu(W{-}Cl)$
		S	14.4	14.2	297vs		
		Cl	15.8	15.8	269vs		
$(Et_4N)_2W_2S_4Cl_8$ (IV)	dark red	C	17.2	18.5	600w	607m	$\nu(S{-}S)$
		H	3.8	4.0	535w		
		N	2.4	2.7	465w	432m	$\delta(W_2S_4)$
		W	35.5	35.4	330vs	330vs	$\nu(W{-}Cl)$
		S	11.7	12.3		320vs	
		Cl	27.1	27.3		192s	$\nu(W{-}W)$
$(Et_4N)_2W_2S_4Br_4$ (V)	green	C	17.5	17.8	528s	529vs	$\nu(W{=}S)$
		H	3.7	3.7	518m	519s	
		N	2.6	2.6	457s	448s	$\delta(W_2S_2)$
		W	34.0	34.0	360m	352s	
		S	11.9	11.9	210s		$\nu(W{-}Br)$
		Br	29.6	29.7	200m		
					165m	186w	$\nu(W{-}W)$
$(Et_4N)_2W_2S_4Br_8$ (VI)	dark red	C	13.2	13.8	584w	598s	$\nu(S{-}S)$
		H	2.8	2.9		335m	$\delta(W_2S_4)$
		N	1.6	2.0		325s	
		W	26.8	26.4		310m	
		S	8.8	9.2	200vs	234m	$\nu(W{-}Br)$
		Br	45.9	45.8		153s	$\nu(W{-}W)$
$W_2S_3Br_6 \cdot 2CH_3CN$ (VIII)	golden	C	5.2	4.7	600w		$\nu(S{-}S)$
		H	0.7	0.6	445w		$\delta(W_2S_3)$
		N	2.7	2.7			
		W	35.9	35.9			
		S	9.4	9.4			
		Br	46.4	46.8			

precipitated solid was filtered off, washed with CH_2Cl_2 and vacuum dried. Yield: 0.62 g of **III**, 39%.

The mother liquor was saturated with HCl for 10 min and the solution was allowed to stay for a week in a closed vessel. The crystals were filtered off and washed with acetonitrile, alcohol and pentane. Yield: 0.15 g of **IV**, 8%.

Preparation of $(Et_4N)_2W_2S_4Br_4$ (V) and $(Et_4N)_2W_2S_4Br_8$ (VI)

HBr was passed through a suspension of $(Et_4N)_2$-WS_4 in CH_2Cl_2 (3.00 g in 150 ml) until the yellow precipitate of the starting complex disappeared and for another 5 min. The precipitate was filtered off, washed with methylene chloride and dried under vacuum. Yield: 1.51 g of **V**, 54%. The mother solution was allowed to stay for a week in a closed vessel. The crystals were treated as in the synthesis of **IV**. Yield: 1.17 g of **VI**, 32%.

Preparation of $(Et_4N)_2W_2S_3Br_8$ (VII) and $(Et_4N)_2W_2S_4Br_8$ (VI)

HBr was passed through a suspension of $(Et_4N)_2$-WS_4 in CH_2Cl_2 (1.00 g in 150 ml). After 15 min the dark red solution was separated from the precipitate and left to stay at room temperature in a closed vessel. The precipitated crystals were filtered off, washed with chloroform and dried under vacuum at 70 °C. Obtained 0.65 g of **VII**, 56%. The mother solution was kept closed for another week. The precipitated crystals were filtered off, washed with acetonitrile, alcohol and pentane. Yield: 0.71 g of **VI**, 19%.

Preparation of $W_2S_3Br_6 \cdot 2CH_3CN$ (VIII) from VII

HBr was passed through a solution of **VII** in CH_3CN (0.50 g in 30 ml). The precipitated crystals having the form of plates were filtered off, washed with acetonitrile, ether and dried under vacuum. Yield 0.31 g of **VIII**, 82%.

Complex **VIII** was obtained in 89% yield also in the reaction of Br_2 with a CH_3CN solution of **VII**.

Preparation of $(Et_4N)_2W_2S_3Br_8$ (VII) from VIII

Complex **VIII** (0.15 g) and Et_4NBr (0.20 g) were boiled in 20 ml of acetonitrile for 15 min. Then 30 ml of ether was added to the dark brown solution; the precipitated solid was filtered off, washed with alcohol, ether and dried under vacuum. Yield: 0.08 g, 40%.

Preparation of $(Et_4N)_2W_2S_4Br_8$ (VI) from VII

Complex **VII** (0.20 g) and sulfur (0.01 g) were boiled in acetonitrile (30 ml). The precipitate was filtered off. Then toluene was added to the filtrate and the solution was kept for 24 h at -20 °C. The crystals were filtered off, washed with toluene, ether and dried under vacuum. Yield: 0.042 g, 21%.

Preparation of $W_2S_3Br_6 \cdot 2CH_3CN$ (VIII) from V

A solution of Br_2 in CH_3CN (0.15 ml in 5 ml) was slowly added dropwise to a suspension of **V** in CH_3CN (0.30 g in 30 ml). First dissolution of the precipitate occurred to form a dark red solution from which, upon further addition of Br_2, a golden yellow precipitate of complex **VIII** was formed. Yield: 0.14 g, 49%.

Results and Discussion

The Interaction of $(Et_4N)_2WS_4$ with HX (X = Cl, Br) in CH_2Cl_2

When dry hydrohalogens HX (X = Cl, Br) are passed into a suspension of $(Et_4N)_2WS_4$ in CH_2Cl_2 at room temperature the colour of the solution rapidly changes from yellow to red–brown, the yellow precipitate of $(Et_4N)_2WS_4$ gradually dissolving. At the moment the precipitate of the starting complex disappeared completely $(Et_4N)_2W_4S_{12} \cdot 2CH_2Cl_2$ (**Ia**) and $(Et_4N)_2W_2S_4Br_4$ (**V**) (reaction with HCl and HBr, respectively) were found in the newly formed precipitate. After separation of **Ia** or **V** $(Et_4N)_2W_3S_9$ (**II**) and $(Et_4N)_2W_2S_4Br_8$ (**VI**) crystallized from the mother solution. According to the IR data the tetranuclear complex **Ia** forms also in the reaction of $(Et_4N)_2WS_4$ with HBr but this complex is difficult to isolate in analytically pure form since it rapidly transforms into **V**.

When complexes **Ia** and **V** are left in the reaction mixture then, with further passing of HX, their precipitates dissolve and $(Et_4N)_2W_2S_4Cl_4$ (**III**) and $(Et_4N)_2W_2S_3Br_8$ (**VII**) crystallize from the resulting solution within 24 h.

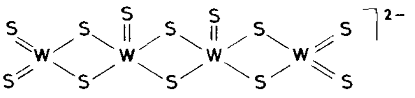
In the reaction with HCl after separation of **III** another binuclear chloride complex, $(Et_4N)_2W_2S_4Cl_8$ (**IV**), forms in a small yield upon prolonged standing of the mother solution. Similarly, in the reaction with HBr after separation of complex **VII**, $(Et_4N)_2W_2S_4Br_8$ (**VI**) is formed in moderate yield.

Thus, methods have been developed which allow preparation of tetranuclear thiocomplex **I** and binuclear thiohalide complexes **III** and **VI** from mononuclear thiocomplex $(Et_4N)_2WS_4$ in a comparatively simple way and in high yields. Attempts to obtain the thiochloride analog of **VII**, $(Et_4N)_2W_2S_3Cl_8$, were unsuccessful. It should be noted that the syntheses are well reproduced if one follows the above procedures.

The Tetranuclear $(Et_4N)_2W_4S_{12}$ (I) Complex

Complexes **I**, **Ia** and **Ib** (Scheme 3) are red–violet crystalline substances not soluble in hydrocarbons, benzene, methylene chloride but readily soluble in acetonitrile, acetone and DMF. The solutions of the complexes slowly decompose in air. When **Ia** was boiled in benzene a solvate of different composition was obtained – $(Et_4N)_2W_4S_{12} \cdot C_6H_6$ (**Ib**). Heating of **Ia** under vacuum produced a non-solvated complex **I** having a deeper colour then the starting solvate. The composition of the solvates was established from elemental analysis and PMR data.

The IR spectra of complexes **I**, **Ia** and **Ib** coincide with that of the $(PPh_4)_2W_4S_{12}$ complex except for the bands due to the PPh_4^+ as well as to CH_2Cl_2 and C_6H_6. We therefore suggest that the $W_4S_{12}^{2-}$ anion of tetraethylammonium salts also has a *syn* configuration as in the tetraphylphosphonium salts [7].



I

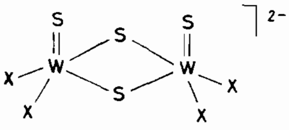
Let us note that the IR and Raman spectra of thiocomplexes in the 600–400 cm^{-1} range are rather characteristic and can be used for identification of these compounds. The bands at 529 (IR) and 537 (Raman) cm^{-1} are essentially due to the $W_{central}=S$ valence vibrations while the bands at 500 (IR) and 507 (Raman) cm^{-1} correspond to the W=S vibrations of the WS_4^{2-} fragment. The deformation vibrations of the W_2S_2 fragments have smaller intensities and frequencies. The very strong bands at 195 and 162 cm^{-1} in the Raman spectra of the complex may be assigned to the W–W vibrations.

The Binuclear $(Et_4N)_2W_2S_4Cl_4$ (III) and $(Et_4N)_2W_2S_4Br_4$ (V) Complexes

The $W_2S_4Cl_4^{2-}$ and $W_2S_4Br_4^{2-}$ complexes have not been described in the literature but they may be compared with the structurally well-characterized complex $W_2S_2O_2Cl_4^{2-}$, prepared by interaction of $WOSCl_2$ with Ph_4AsCl [9], as well as with $W_2S_4(py)_4$-

Br_2 [10], $W_2S_4(S_2CNEt_2)_2$, $W_2S_4(S_2P(OEt)_2)_2$ [11] and $W_4S_{12}^{2-}$ [7] containing the $[S{=}W(\mu_2\text{-}S)_2W{=}S]^{2+}$ fragments.

We believe that the $W_2S_4X_4^{2-}$ (X = Cl, Br) anions of complexes **III** and **V** have the following structure



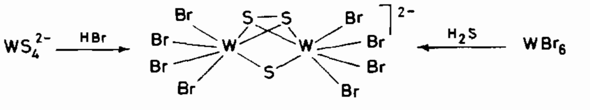
III (X = Cl)
V (X = Br)

Thus complexes **III** and **V** react with sodium diethyldithiocarbamate producing, while retaining their central $[S{=}W(\mu_2\text{-}S)_2W{=}S]^{2+}$ fragment, the known complex $W_2S_4(S_2CNEt_2)_2$ [11].

The vibrational spectra of **III** and **V** in the region of valence and deformation vibrations involving tungsten and sulfur atoms coincide with each other and are identical to the vibrational spectra of the known thiocomplexes of tungsten containing the $[S{=}W(\mu_2\text{-}S)_2W{=}S]^{2+}$ [7, 10, 11].

The Binuclear $(Et_4N)_2W_2S_3Br_8$ (VII) Complex

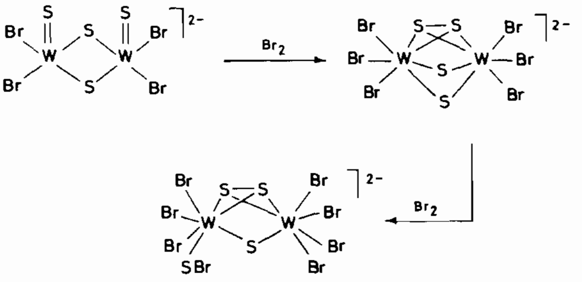
The binuclear thiobromide complex $(Et_4N)_2W_2S_3Br_8$ (**VII**) has the form of dark brown lustrous plates and is unstable in air. This complex may be compared with the structurally well-characterized complex $(Ph_4P)_2W_2S_3Br_8 \cdot H_2S \cdot CH_2Cl_2$ which has been obtained by interacting WBr_6 with H_2S in CH_2Cl_2 in the presence of Ph_4PBr [12].



VII

The IR spectrum of **VII** in the 630–100 cm^{-1} range coincides with that of the tetraphenylphosphonium salt.

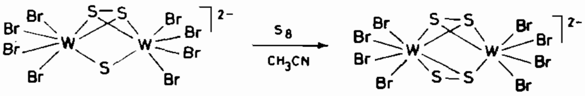
Passing of HBr through an acetonitrile solution of **VII** or addition of Br_2 results in the formation of a golden precipitate, the $W_2S_3Br_6 \cdot 2CH_3CN$ complex (**VIII**) (Scheme 4). The same complex is obtained when by interaction of Br_2 with a solution of the binuclear thiobromide complex $(Et_4N)_2W_2S_4Br_4$ (**V**). Under the reaction conditions re-arrangement of the central metallocluster fragment $[S{=}W(\mu_2\text{-}S)_2W{=}S]^{2+}$ takes place. A possible scheme for this interesting rearrangement is as follows



Addition of a Br_2 molecule at the two tungsten atoms of **VII** induces the intramolecular transfer of electrons from the terminal sulfur atoms ($2S^{2-} - 2e \rightarrow S_2^{2-}$) via the tungsten atoms to the bromine atoms ($Br_2 + 2e \rightarrow 2Br^-$) followed by insertion of Br_2 at one of the W–μ_2-S bonds with subsequent elimination of SBr_2.

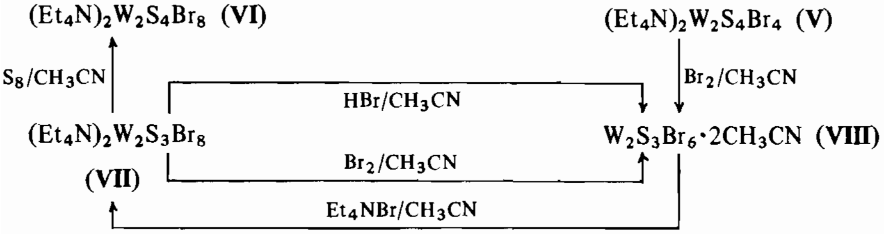
The Binuclear $(Et_4N)_2W_2S_4Cl_8$ (IV) and $(Et_4N)_2W_2S_4Br_8$ (VI) Complexes

The binuclear thiohalide complexes of tungsten $(Et_4N)_2W_2S_4X_8$ slowly crystallize from the mother solutions obtained after separation of the precipitates of complexes **III**, **V** or **VII** in the reactions of $(Et_4N)_2WS_4$ with HX in CH_2Cl_2 (Schemes 1 and 2). Moderate yields of the thiobromide complex **VI** are also obtained when complex **VII** is boiled with elemental sulfur in acetonitrile (Scheme 4).



VII **VI**

Complexes **IV** and **VI**, dark red crystals, are soluble in acetonitrile, DMF and insoluble in hydrocarbons, aromatic and chlorinated hydrocarbons and alcohols. The complexes are diamagnetic and isostructural with each other according to the X-ray powder diffraction data. (Complex **VI**: $a = 7.466$; $b = 11.610$; $c = 19.456$ Å; $\beta = 89.67°$; Complex **IV**: $a = 7.193$; $b = 11.396$; $c = 18.80$ Å; $\beta = 89.20°$). The bands of the valence



Scheme 4. Reactions of binuclear complexes.

vibrations of the S_2 ligand are weak in the IR spectra and strong in the Raman spectra.

The structure of complex **VI** has been established by Virovetz by X-ray structural analysis of the monocrystal [13]. The structure of the $W_2S_4Br_8^{2-}$ anion in complex **VI** is analogous to that described for the $Mo_2S_4X_8^{2-}$ anions (X = Cl, Br) [14]. The anion contains eight terminal bromine atoms and two S_2^{2-} moieties (the S–S bond distance is 2.004(2) Å) which are coordinated by the acetylene type symmetrically with respect to the two tungsten atoms. The W–W distance in this 34-electron complex is equal to 2.8345(5) Å which corresponds to a single W–W bond.

A Possible Mechanism of Reaction of $(Et_4N)_2WS_4$ with HX (X = Cl, Br) in CH_2Cl_2

High lability of the systems containing tetrathiotungstate ions and an acid leads to various products when one varies the reactants concentration and reaction time, changes the cation, acid or solvent. For example, $(PPh_4)_2WS_4$, $(Bu_4N)_2WS_4$ in CH_2Cl_2 and $CHCl_3$ readily interact with HCl or HBr, but complexes analogous to **I–VII** have not been obtained.

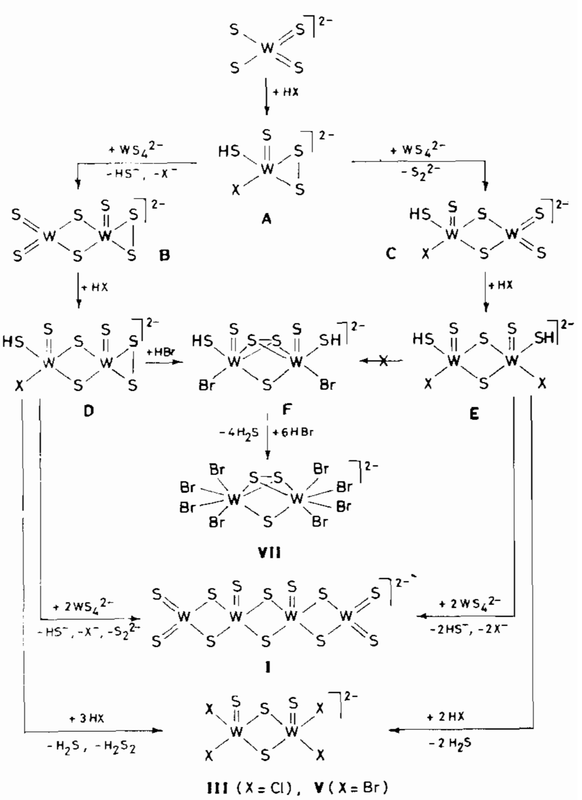
In the reactions of $(Et_4N)_2WS_4$ with HCl and HBr in CH_2Cl_2 there are at least two factors that are noteworthy: (i) a low solubility of $(Et_4N)_2WS_4$ in methylene chloride which ensures a low concentration of WS_4^{2-} in the solution; the reaction may be heterogeneous. (ii) HCl and HBr practically do not dissociate in methylene chloride.

The first stage appears to involve addition of HX (X = Cl, Br) to the tetrathiotungstate ion (Scheme 5). This induces intramolecular transfer of electrons from the sulfur atom to tungsten resulting in reduction of the metal atom ($W^{6+} + 2e^- \rightarrow W^{4+}$) and formation of a complex with a S_2^{2-} ligand ($2S^{2-} - 2e^- \rightarrow S_2^{2-}$).

Nucleophilic substitution of S_2^{2-} or HS^- and X^- in **A** by the tetrathiometallate ion leads to binuclear complexes **B** and **C**, respectively, which also add HX at the W=S bond. The resulting intermediates **D** and **E** may react in two ways: to form either $W_4S_{12}^{2-}$ (under the conditions when WS_4^{2-} is still left) or $W_2S_4X_4^{2-}$ (when all the WS_4^{2-} is used up).

Addition of H^+ at μ_2-S of the intermediate **D** (but not of **E**) should lead to a weakening of the donor ability of this ligand and a rearrangement resulting in the formation of complex **F** with a μ_2S_2 ligand. Further substitution of the terminal ligands S^{2-}, SH^-, probably through a series of addition–elimination processes, results in formation of $W_2S_3Br_8^{2-}$. It should be also noted that protonation of μ_2-S in the binuclear complex $(Ph_4P)_2W_2S_{11}$ has been recently shown to result in a change in the complex geometry and formation of a semibridging S_2 ligand [2, 3].

In conclusion it should be noted that the binuclear $W_2S_4X_4^{2-}$ should not be considered as a precursor of $W_4S_{12}^{2-}$. Thus in the reaction of **III** with two equivalents of $(Et_4N)_2WS_4$ only the trinuclear thiocomplex $(Et_4N)_2W_3S_9$ was obtained and no complex **I** was observed. Also, the reaction of **I** with HCl in methylene chloride produced no complex **III**.



Scheme 5. Tentative scheme for generation and interconversion of the thiotungstate anions.

Acknowledgements

The authors thank Dr B. A. Kolesow for recording the Raman spectra and Dr V. N. Ikorskii for magnetic susceptibility measurements.

References

1 A. Müller, E. Diemann, R. Jostes and H. Bögge, *Angew. Chem., Int. Ed. Engl., 20* (1981) 934.
2 J. M. Manoli, C. Potvin and F. Secheresse, *Inorg. Chem., 26* (1987) 340.
3 F. Secheresse, J. M. Manoli and C. Potvin, *Inorg. Chem., 25* (1986) 3367.
4 A. Müller, W. Rittner, A. Neumann, E. Königer-Ahlborn and R. G. Bhattacharyya, *Z. Anorg. Allg. Chem., 461* (1980) 91.
5 R. W. M. Wardle, S. Bhaduri, Ch.-N. Chau and J. A. Ibers, *Inorg. Chem., 27* (1988) 1747.
6 K. Hanewald, G. Kiel and G. Gattow, *Z. Anorg. Allg. Chem., 478* (1981) 215.

7 F. Secheresse, J. Lefebvre, J. C. Daran and Y. Jeannin, *Inorg. Chem., 21* (1982) 1311.

8 J. M. McDonald, C. D. Friesen, L. D. Rosenheim and W. E. Newton, *Inorg. Chim. Acta, 72* (1983) 205.

9 M. G. B. Drew, E. M. Page and D. A. Rice, *Inorg. Chim. Acta, 76* (1983) 33.

10 M. G. B. Drew, R. J. Hobson, D. A. Rice and N. Turp, *J. Chem. Soc., Dalton Trans.,* (1986) 2165.

11 S. A. Cohen and E. I. Stiefel, *Inorg. Chem., 24* (1985)
1 4657.

12 P. Klingelhöfer and U. Müller, *Z. Anorg. Allg. Chem., 542* (1986) 7.

13 A. V. Virovetz, *Mater. Vses. Nauchn. Stud. Conf. Khim., 1988*, p. 33.

14 D. Fenske, B. Czeska, C. Schumacher, R. E. Schmidt and K. Dehnike, *Z. Anorg. Allg. Chem., 520* (1985) 7.