

## Reactions of Polynuclear Thio- and Oxothiocomplexes of Molybdenum and Tungsten with Co(II), Ni(II), Cu(I) and Au(I) Chlorides

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### Abstract

Reactions of some polynuclear thio- and oxothiocomplexes of molybdenum and tungsten with Co(II), Ni(II), Cu(I) and Au(I) chlorides have been studied. Interaction of  $(Et_4N)_2W_3S_9$  and  $(Et_4N)_2W_4S_{12}$  with  $Ph_3PMCl$  ( $M = Cu, Au$ ) is accompanied by elimination of  $WS_4^{2-}$  fragments giving rise to the heterometallic thiocomplexes  $(Ph_3P)_3Cu_2WS_4$  and  $(Ph_3P)_2Au_2WS_4$ . The latter complex has been obtained in quantitative yield in the reaction of mononuclear  $WS_4^{2-}$  with  $Ph_3PAuCl$  or  $[(Ph_3PAu)_3O]BF_4$ .

The binuclear oxothiocomplex  $(Bu_4N)_2Mo_2S_7O$  interacts with Co, Ni and Cu chlorides to form amorphous thiocomplexes  $(Bu_4N)Cu(Mo_2S_7O)$  and  $(Bu_4N)_2M(Mo_2S_7O)_2$  ( $M = Co, Ni$ ). According to IR data the  $(Mo_2S_7O)^{2-}$  fragment remains intact in these complexes.

Polynuclear thiocomplexes can also act as a source of sulfur with respect to weak Lewis acids. Reaction of the heterometallic thiocomplex  $(Ph_3P)_2Au_2WS_4$  with a source of electrophilic particles  $Ph_3PAu^+$  results in complete desulfuration of the thiocomplex and formation of  $[(Ph_3PAu)_3S]BF_4$  in high yield.

### Introduction

Mononuclear tetrahedral thioanions  $MoS_4^{2-}$  and  $WS_4^{2-}$  are capable of coordinating several atoms of transition or posttransition metals which results in a large variety of linear, cyclic and skeleton structures with metal–metal interactions [1, 2]. Thiocomplexes of Fe, Co, Ni and Cu have been studied most particularly. Iron complexes are essential for understanding

the structure and mechanism of action of nitrogenase enzyme [3]; complexes of copper are studied in connection with the problem of copper–molybdenum antagonism [4]. Complexes of cobalt and nickel can find application in the synthesis of petroleum hydrodesulfurisation catalysts [5]. At the same time the literature contains no information concerning the use of such polynuclear thio- and oxothiocomplexes as ligands. The present work is a study of complexation reactions of some polynuclear thio- and oxothiocomplexes of molybdenum and tungsten with Co(II), Ni(II), Cu(I) and Au(I) chlorides.

### Experimental

#### Compounds

$(Et_4N)_2W_3S_9$  [6],  $(Et_4N)_2WS_4$  [7],  $(Bu_4N)_2MoS_4$  [7],  $Ph_3PCuCl$  [8],  $Ph_3PAuCl$  [8] and  $[(Ph_3PAu)_3O]BF_4$  [9] were synthesised according to the procedures described in the cited references. For  $(Bu_4N)_2Mo_2S_7O$  and  $(Et_4N)_2W_4S_{12}$  new procedures have been developed. Benzene and toluene were distilled over Na, methylene chloride and  $CH_3CN$  over  $P_4O_{10}$ , and THF and ether over sodium-benzophenone.

#### Characterisation Methods

IR spectra were recorded on a IFS-113 (Bruker) Fourier spectrometer. Raman spectra were obtained on a DFS-24 instrument at an angle of  $90^\circ$  by excitation with 441.5 and 632.8 nm lines of He–Cd and He–Ne lasers. The effective magnetic moments were determined from magnetic susceptibility data by the relative Faraday method taking into account diamagnetism. PMR spectra were recorded on a T-60 instrument (Varian) at a working frequency of 60 MHz with TMS as internal standard. Metals and sulfur were determined by weight methods in the form of

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MoO<sub>2</sub>(C<sub>9</sub>H<sub>6</sub>ON)<sub>2</sub>, WO<sub>3</sub>, Ni(C<sub>4</sub>H<sub>5</sub>N<sub>4</sub>O<sub>4</sub>)<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub> or Co(C<sub>10</sub>H<sub>6</sub>NO<sub>2</sub>)<sub>3</sub>·2H<sub>2</sub>O, CuSCN and BaSO<sub>4</sub>. Determination of carbon and hydrogen was performed in the laboratory of Microanalysis of the Institute of Inorganic Chemistry of the Siberian Branch of the U.S.S.R. Academy of Sciences.

#### Preparation of (Bu<sub>4</sub>N)<sub>2</sub>Mo<sub>2</sub>S<sub>7</sub>O

(Bu<sub>4</sub>N)<sub>2</sub>MoS<sub>4</sub> (13.0 g) was dissolved in 100 ml ethanol upon heating in air and the solution was allowed to stay for a week in an open flask. The dark red precipitate was filtered off, washed with cold ethanol and ether and dried *in vacuo*. Yield, 40%.

*Anal.* Calc. for C<sub>32</sub>H<sub>72</sub>N<sub>2</sub>Mo<sub>2</sub>S<sub>7</sub>O: C, 41.9; H, 7.9; N, 3.1; Mo, 20.9; S, 24.5. Found: C, 41.8; H, 7.7; N, 3.1; Mo, 21.4; S, 24.9%. IR (KBr): 950vs, ν(Mo=O); 530s, ν(S–S); 520s, ν(Mo=S); 462s, δ(Mo<sub>2</sub>S<sub>2</sub>). Raman: 942m, ν(Mo=O); 530s, ν(S–S); 516m, ν(Mo=S); 493m, 424m, 363m, 351s, 324m, 272w.

#### Preparation of (Et<sub>4</sub>N)<sub>2</sub>W<sub>4</sub>S<sub>12</sub>·2CH<sub>2</sub>Cl<sub>2</sub>

(a) One ml of 48% HBr was added to a suspension of 1.5 g (Et<sub>4</sub>N)<sub>2</sub>WS<sub>4</sub> in 75 ml CH<sub>2</sub>Cl<sub>2</sub>. After vigorous stirring for 1 h the resulting red-violet precipitate was filtered, washed successively with water, ethanol, CH<sub>2</sub>Cl<sub>2</sub>, and dried *in vacuo* (30 mm Hg). Yield 0.80 g (80%).

(b) Using a procedure similar to that of (a) 1.0 g (c. 90%) (Et<sub>4</sub>N)<sub>2</sub>W<sub>4</sub>S<sub>12</sub> was obtained from 2.0 g (Et<sub>4</sub>N)<sub>2</sub>WS<sub>4</sub> and 1 ml 38% HCl.

*Anal.* Calc. for C<sub>18</sub>H<sub>44</sub>N<sub>2</sub>Cl<sub>4</sub>W<sub>4</sub>S<sub>12</sub>: C, 13.9; H, 2.8; N, 1.7; W, 47.1; S, 24.8. Found: C, 13.9; H, 2.8; N, 1.8; W, 47.4; S, 25.0%. IR (KBr): 733m, ν(C–Cl); 690w, ν(C–Cl); 529s, ν(W=S); 500s, ν(W=S); 464s, δ(W<sub>2</sub>S<sub>2</sub>); 448m, δ(W<sub>2</sub>S<sub>2</sub>); 310w, 300m, 270m. Raman: 537m, ν(W=S); 507s, ν(W=S); 452m, δ(W<sub>2</sub>S<sub>2</sub>); 313s, 282w, 197vs.

#### Preparation of (Ph<sub>3</sub>P)<sub>3</sub>Cu<sub>2</sub>WS<sub>4</sub>·2CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub> (I)

A solution of 1.31 g Ph<sub>3</sub>PCuCl in 25 ml CH<sub>2</sub>Cl<sub>2</sub> was added to a suspension of 2.00 g (Et<sub>4</sub>N)<sub>2</sub>W<sub>3</sub>S<sub>9</sub> in 40 ml CH<sub>2</sub>Cl<sub>2</sub>. The resulting solution was stirred during 1 h, filtered off and evaporated. The precipitate was extracted with 70 ml of toluene and the extract cooled down to –5 °C. The bright yellow precipitate was filtered off and recrystallised from toluene. Yield 0.50 g (40%). The substance is insoluble in CH<sub>3</sub>CN, readily soluble in CH<sub>2</sub>Cl<sub>2</sub>, moderately soluble in benzene and toluene, melting point (m.p.) 240 °C (dec.).

*Anal.* Calc. for C<sub>68</sub>H<sub>61</sub>P<sub>3</sub>WCu<sub>2</sub>S<sub>4</sub>: C, 58.0; H, 4.3; S, 9.1; W, 13.1; Cu, 9.9. Found: C, 59.4; H, 4.3; S, 8.8; W, 13.0; Cu, 9.6%.

#### Preparation of (Ph<sub>3</sub>P)<sub>2</sub>Au<sub>2</sub>WS<sub>4</sub>·1.5C<sub>6</sub>H<sub>6</sub> (IIa)

(a) From (Et<sub>4</sub>N)<sub>2</sub>W<sub>3</sub>S<sub>9</sub>. To a solution of 0.44 g (Et<sub>4</sub>N)<sub>2</sub>W<sub>3</sub>S<sub>9</sub> in 50 ml CH<sub>3</sub>CN 0.40 g Ph<sub>3</sub>PAuCl was added. After stirring for 40 min the suspension was

filtered and the solid extracted with hot benzene. Then the filtrate was treated with pentane and cooled to –5 °C. The citrus yellow precipitate was filtered, washed with pentane and dried. Yield 0.30 g (90%), m.p. 235 °C (dec.).

*Anal.* Calc. for C<sub>39</sub>H<sub>33</sub>P<sub>2</sub>Au<sub>2</sub>WS<sub>4</sub>: C, 40.0; H, 2.8; P, 4.7. Found: C, 39.3; H, 2.6; P, 4.9%. IR (Nujol) 445vs, δ(AuWS<sub>2</sub>). <sup>1</sup>H NMR (60 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.16; 7.19; 7.23(m, 30 H, PPh<sub>3</sub>); 7.42(s, 9 H, C<sub>6</sub>H<sub>6</sub>).

(b) From (Et<sub>4</sub>N)<sub>2</sub>W<sub>4</sub>S<sub>12</sub>. From 0.31 g (Et<sub>4</sub>N)<sub>2</sub>W<sub>4</sub>S<sub>12</sub> and 0.40 g Ph<sub>3</sub>PAuCl complex IIa was obtained in quantitative yield analogously to (a). Then 0.10 g of sodium diethyldithiocarbamate was added to the mother liquor. NaCl precipitate was filtered off, the filtrate evaporated and reprecipitated with ether from CHCl<sub>3</sub>. The IR spectrum of the orange substance was identical to that of W<sub>2</sub>S<sub>4</sub>[(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCS<sub>2</sub>]<sub>2</sub> [10].

(c) From (Et<sub>4</sub>N)<sub>2</sub>WS<sub>4</sub> and Ph<sub>3</sub>PAuCl. To a solution of 0.50 g Ph<sub>3</sub>PAuCl in CHCl<sub>3</sub> a solution of 0.30 g (Et<sub>4</sub>N)<sub>2</sub>WS<sub>4</sub> in water was added. After stirring for 15 min the organic layer was separated, treated with K<sub>2</sub>CO<sub>3</sub>, evaporated to dryness and recrystallised from benzene. Yield 98%.

(d) From (Me<sub>4</sub>N)<sub>2</sub>WS<sub>4</sub> and [(Ph<sub>3</sub>PAu)<sub>3</sub>O]BF<sub>4</sub>. To a solution of 0.31 g (Me<sub>4</sub>N)<sub>2</sub>WS<sub>4</sub> in 8 ml of water 5 ml THF and 1.00 g [(Ph<sub>3</sub>PAu)<sub>3</sub>O]BF<sub>4</sub> were added under intense stirring. After 3 h the precipitate was filtered off and reprecipitated with ether from benzene in quantitative yield. Recrystallisation of II from CHCl<sub>3</sub> produces (Ph<sub>3</sub>P)<sub>2</sub>Au<sub>2</sub>WS<sub>4</sub>·CHCl<sub>3</sub> solvate.

*Anal.* Calc. for C<sub>37</sub>H<sub>33</sub>P<sub>2</sub>Cl<sub>3</sub>WAu<sub>2</sub>S<sub>4</sub>: C, 32.9; H, 2.8. Found: C, 33.4; H, 2.8%.

#### Preparation of [(Ph<sub>3</sub>PAu)<sub>3</sub>S]BF<sub>4</sub>

(a) 0.20 g (Ph<sub>3</sub>P)<sub>2</sub>Au<sub>2</sub>WS<sub>4</sub> and 0.32 g [(Ph<sub>3</sub>PAu)<sub>3</sub>O]BF<sub>4</sub> were stirred for 16 h in THF to the disappearance of the qualitative reaction to oxonium [9]. The white precipitate was filtered off, washed with THF and dried. Yield c. 100%. IR (Nujol): 1107m, 1065s, 1003w, 810w, 735w, 715s, 705w, 539vs, 512s, 520sh [11].

(b) A solution of Ph<sub>3</sub>PAuBF<sub>4</sub> prepared from 0.55 g of AgBF<sub>4</sub>·3(O<sub>2</sub>C<sub>4</sub>H<sub>8</sub>) and 0.58 g of Ph<sub>3</sub>PAuCl in 25 ml THF was added to a solution of 0.15 g (Ph<sub>3</sub>P)<sub>2</sub>Au<sub>2</sub>WS<sub>4</sub> in 50 ml THF. The solution was stirred for 48 h and allowed to stay overnight at –5 °C. The precipitate was extracted with CHCl<sub>3</sub>, then a triple volume of pentane was added to the extract and the solution cooled down to –5 °C. The precipitate was filtered off. Yield 0.55 g (80%).

#### Interaction of FcHgCl with (Et<sub>4</sub>N)<sub>2</sub>W<sub>3</sub>S<sub>9</sub>

FcHgCl (0.23 g) was added to a solution of 0.30 g (Et<sub>4</sub>N)<sub>2</sub>W<sub>3</sub>S<sub>9</sub> in 20 ml of acetonitrile. The solution was boiled for 30 min, the black precipitate filtered off and the filtrate evaporated *in vacuo*. The residue was extracted with *m*-xylene and evaporated. The

orange substance has been identified by the TLC method to be a mixture of FcH and Fc<sub>2</sub> (Silufol, pentane),  $R_f$ : Fc<sub>2</sub> = 0.11; FcH = 0.72.

#### Preparation of (Bu<sub>4</sub>N)Cu(Mo<sub>2</sub>S<sub>7</sub>O) (III)

(a) From CuCl. To a solution of 0.70 g (Bu<sub>4</sub>N)<sub>2</sub>Mo<sub>2</sub>S<sub>7</sub>O in 20 ml of CH<sub>3</sub>CN 0.09 g of CuCl was added under intense stirring. After 40 min 60 ml of ethanol was added to the brown solution. The precipitate was filtered, washed with hot ethanol, ether and dried *in vacuo*. Yield 0.50 g (90%) of black X-ray amorphous powder III.

*Anal.* Calc. for C<sub>16</sub>H<sub>36</sub>NOMo<sub>2</sub>CuS<sub>7</sub>: C, 25.9; H, 4.9; N, 1.9; Mo, 25.9; Cu, 8.6; S, 30.3. Found: C, 24.6; H, 4.9; N, 1.8; Mo, 25.7; Cu, 9.0; S, 30.2%. IR (KBr): 955vs,  $\nu$ (Mo=O); 513m,  $\nu$ (S-S, Mo=S), 460s,  $\delta$ (Mo<sub>2</sub>S<sub>2</sub>). Molar conductivity 270 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> (DMF).

(b) Analogously, reaction of 0.36 g (Bu<sub>4</sub>N)<sub>2</sub>Mo<sub>2</sub>S<sub>7</sub>O and 0.22 g Ph<sub>3</sub>PCuCl produced 0.30 g of complex III.

#### Preparation of (Bu<sub>4</sub>N)<sub>2</sub>Ni(Mo<sub>2</sub>S<sub>7</sub>O)<sub>2</sub> (IV)

To a solution of 0.70 g (Bu<sub>4</sub>N)<sub>2</sub>Mo<sub>2</sub>S<sub>7</sub>O in 20 ml CH<sub>3</sub>CN a solution of 0.10 g NiCl<sub>2</sub>·6H<sub>2</sub>O in 20 ml of ethanol was added and stirred for 1 h. The precipitate was filtered from the colourless solution, washed with ethanol, ether and dried *in vacuo*. Yield 0.50 g (90%) of brown X-ray amorphous powder IV.

*Anal.* Calc. for C<sub>32</sub>H<sub>72</sub>N<sub>2</sub>O<sub>2</sub>Mo<sub>4</sub>NiS<sub>14</sub>: C, 27.3; H, 5.1; N, 2.1; Mo, 27.3; Ni, 4.2; S, 31.9. Found: C, 27.0; H, 4.8; N, 1.6; Mo, 28.2; Ni, 4.1; S, 32.0%. IR (KBr): 947vs,  $\nu$ (Mo=O), 520s,  $\nu$ (Mo=S, S-S), 467m,  $\delta$ (Mo<sub>2</sub>S<sub>2</sub>).  $\Lambda_m$ (DMF) = 299 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

#### Preparation of (Bu<sub>4</sub>N)<sub>2</sub>Co(Mo<sub>2</sub>S<sub>7</sub>O)<sub>2</sub> (V)

Using procedures identical to those described for IV, complex V was prepared from (Bu<sub>4</sub>N)<sub>2</sub>Mo<sub>2</sub>S<sub>7</sub>O and CoCl<sub>2</sub>·6H<sub>2</sub>O in 60% yield.

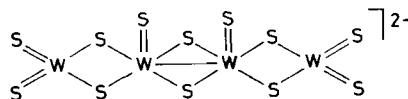
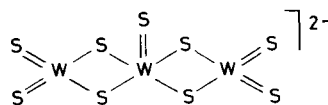
*Anal.* Calc. for C<sub>32</sub>H<sub>72</sub>N<sub>2</sub>O<sub>2</sub>Mo<sub>4</sub>CoS<sub>14</sub>: C, 27.3; H, 5.1; N, 2.0; Mo, 27.3; Co, 4.2; S, 31.9. Found: C, 27.0; H, 5.1; Mo, 27.3; N, 1.6; Co, 4.4; S, 31.6%. The IR spectrum and molar conductivity of V are identical to those of complex IV.

## Results and Discussion

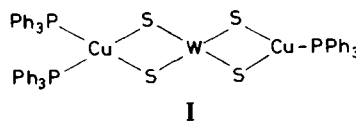
#### Reactions of (Et<sub>4</sub>N)<sub>2</sub>W<sub>3</sub>S<sub>9</sub> and (Et<sub>4</sub>N)<sub>2</sub>W<sub>4</sub>S<sub>12</sub> with Ph<sub>3</sub>PMCl (M = Cu, Au)

In the polynuclear complexes W<sub>3</sub>S<sub>9</sub><sup>2-</sup> and W<sub>4</sub>S<sub>12</sub><sup>2-</sup> the metal atoms of central fragments (W=S)<sup>2+</sup> and [S=W( $\mu_2$ -S)W=S]<sup>2+</sup> are coordinated by two tetra-thiometallate ions WS<sub>4</sub><sup>2-</sup> [12, 13].

Reaction of Ph<sub>3</sub>PCuCl with (Et<sub>4</sub>N)<sub>2</sub>W<sub>3</sub>S<sub>9</sub> and (Et<sub>4</sub>N)<sub>2</sub>W<sub>4</sub>S<sub>12</sub> proceeds in a complex manner giving rise to at least two reaction products: (Ph<sub>3</sub>P)<sub>3</sub>Cu<sub>2</sub>WS<sub>4</sub>(I) and (Ph<sub>3</sub>P)<sub>3</sub>(Cu<sub>3</sub>WS<sub>4</sub>Cl). In both reactions

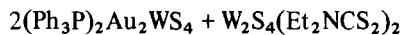


complex I has been isolated as a solvate with toluene, (Ph<sub>3</sub>P)<sub>3</sub>Cu<sub>2</sub>WS<sub>4</sub>·2CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>, in 40% yield. In an earlier study [14] a solvate of the composition (Ph<sub>3</sub>P)<sub>3</sub>Cu<sub>2</sub>WS<sub>4</sub>·0.8CH<sub>2</sub>Cl<sub>2</sub> has been obtained in the reaction of mononuclear complex (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> with PPh<sub>3</sub> and CuCl<sub>2</sub>·2H<sub>2</sub>O in methylene chloride for which X-ray diffraction data indicated the following structure [14].

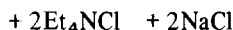


Coincidence of the vibrational spectra for the complex obtained in the present study and that of ref. 14 suggests that they have the same structure. In addition to complex I, the reaction of (Et<sub>4</sub>N)<sub>2</sub>W<sub>3</sub>S<sub>9</sub> and (Et<sub>4</sub>N)<sub>2</sub>W<sub>4</sub>S<sub>12</sub> with Ph<sub>3</sub>PCuCl also produced a small amount of single crystals (<5%) whose unit cell parameters were found to coincide with those of the cluster (Ph<sub>3</sub>P)<sub>3</sub>[Cu<sub>3</sub>WS<sub>4</sub>]Cl [14] prepared from mononuclear WS<sub>4</sub><sup>2-</sup>.

The Ph<sub>3</sub>PAuCl complex interacts with solutions of complexes (Et<sub>4</sub>N)<sub>2</sub>W<sub>3</sub>S<sub>9</sub> and (Et<sub>4</sub>N)<sub>2</sub>W<sub>4</sub>S<sub>12</sub> at room temperature producing (Ph<sub>3</sub>P)<sub>2</sub>Au<sub>2</sub>WS<sub>4</sub> (II) in high yield. In the reaction with W<sub>4</sub>S<sub>12</sub><sup>2-</sup>, addition of (Et<sub>2</sub>NCS<sub>2</sub>)Na to the mother liquor after separation of II led to isolation of the diethyldithiocarbamate complex of tungsten, W<sub>2</sub>S<sub>4</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>. This fact indicates that the central fragment W<sub>2</sub>S<sub>4</sub><sup>2+</sup> is preserved in the reaction

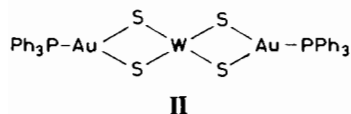


II



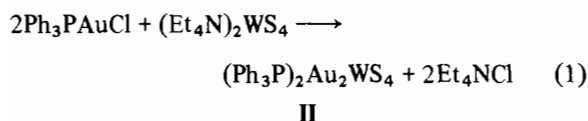
Complex II was obtained as solvates with benzene and chloroform. They are citrus yellow crystalline substances readily soluble in weakly polar solvents and having a sufficiently high thermal stability (dec. >235 °C). Concentrated hydrochloric acid destructs II upon heating to form Ph<sub>3</sub>PAuCl and tungsten trisulfide. IR spectra of II show bands of a

coordinated  $\text{Ph}_3\text{P}$  and an intense band at  $445\text{ cm}^{-1}$  characteristic of vibrations involving  $\mu_2$ -sulfur atoms ( $\delta(\text{WS}_2\text{Au})$ ). We proposed the following structure for **II**.

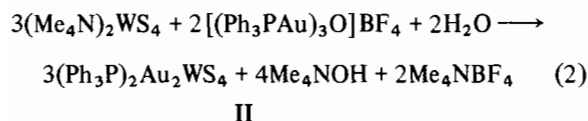


Thiometallate complexes of gold are much less studied than their copper and silver analogs and differ from them in composition. Only  $(\text{Ph}_2\text{MeP})_2\text{Au}_2\text{WS}_4$  [15] and  $(\text{Ph}_3\text{P})_2\text{Au}_2\text{MoS}_4$  [16] have been described and structurally characterised. These complexes have been obtained by reaction of  $\text{R}_3\text{PAuCl}$  with the salts of  $\text{WS}_4^{2-}$  and  $\text{MoS}_4^{2-}$ . Differences in stoichiometry between the complexes of copper and gold are due to the trend of the latter to lower coordination numbers. Complexes of three- and the more so four-fold coordinated gold are rather rare [17].

To verify the proposed structure of **II** the complex has been prepared by an alternative synthesis according to reaction (1)



High yields of complex **II** have also been obtained in the reaction of the oxonium salt  $[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$  with the mononuclear complex:

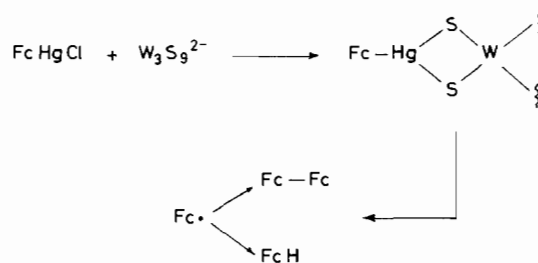


It should be noted that complexes **I** and **II** can be chromatographed on aluminium oxide without decomposition, a feature that is convenient to use for their purification and detection.

The sulfur atoms of the trinuclear thiocomplex **II** are capable of coordinating extra metal atoms on account of the unshared electron pairs. We made an attempt to use this potential property to synthesise large clusters, making use of  $[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$  and  $\text{Ph}_3\text{PAuBF}_4$  as the sources of electrophilic particles,  $\text{Ph}_3\text{PAu}^+$ . It turned out, however, that interaction of the trinuclear heterometallic complex **II** with these gold compounds leads in both cases to elimination of sulfur and formation of the sulfonium complex  $[(\text{Ph}_3\text{PAu})_3\text{S}]\text{BF}_4$ . The fate of the tungsten could not be followed. The reaction with  $\text{Ph}_3\text{PAuBF}_4$  is accompanied by elimination of four sulfur atoms from **II** and requires 10 equivalents of the reagent per one equivalent of **II**.

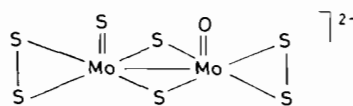
Thus, interaction of  $(\text{Et}_4\text{N})_2\text{W}_3\text{S}_9$  and  $(\text{Et}_4\text{N})_2\text{W}_4\text{S}_{12}$  with  $\text{Ph}_3\text{PCuCl}$  and  $\text{Ph}_3\text{PAuCl}$  proceeds via elimination of  $\text{WS}_4^{2-}$  fragments with subsequent coordination to them of Cu and Au atoms. These reactions can be considered as a transfer of  $\text{WS}_4^{2-}$  ligands from  $(\text{W}=\text{S})^{2+}$  and  $(\text{W}_2\text{S}_4)^{2+}$  fragments to  $\text{Ph}_3\text{PCu}^+$  and  $\text{Ph}_3\text{PAu}^+$ . The polynuclear thiocomplexes can also act as sources of sulfur with respect to weak Lewis acids, such as  $\text{Ph}_3\text{PAu}^+$ .

Taking into account the fact that the organomercury compounds are isostructural and isoelectronic with complexes of Au(I) we have studied the interaction of  $(\text{Et}_4\text{N})_2\text{W}_3\text{S}_9$  with  $\text{FcHgCl}$ . But in this reaction we were able to isolate only ferrocene and diferrocenyl and could not obtain any stable heterometallic species. It appears that first a complex with a thiometallate ligand is formed in the reaction which decomposes under the reaction conditions to form  $\text{HgS}$  and ferrocenyl radical.

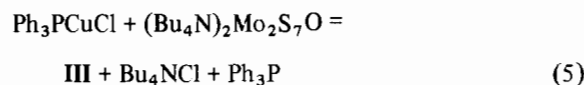
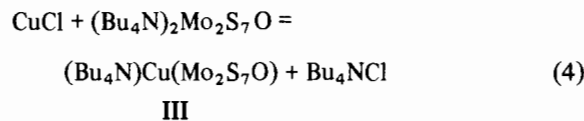


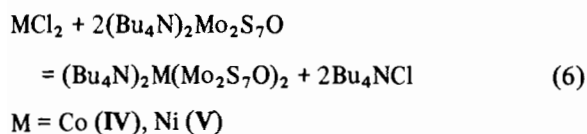
#### Reactions of $(\text{Bu}_4\text{N})_2\text{Mo}_2\text{S}_7\text{O}$ with Co(II), Ni(II) and Cu(I) Chlorides

The binuclear oxothiocomplex of molybdenum  $(\text{Bu}_4\text{N})_2\text{Mo}_2\text{S}_7\text{O}$  contains no tetrathiometallate fragment  $\text{MoS}_4^{2-}$  [18]. This substance contains the  $[\text{Mo}_2(\mu_2\text{-S})_2(\text{O})(\text{S})]^{2+}$  core coordinated by two  $\text{S}_2^{2-}$  ligands.



The reaction of  $\text{Mo}_2\text{S}_7\text{O}^{2-}$  with Co(II), Ni(II) and Cu(I) chlorides proceeds readily already at room temperature producing heterometallic thiocomplexes **III–V**.





Elimination of  $\text{PPh}_3$  in reaction (5) was indicated by the TLC data. This is one of the few examples of the elimination of a coordinated phosphine in the chemistry of Cu(I) complexes. Complexes IV and V are formed even with a ten-fold excess of metal chloride.

Complexes III–V are black or dark brown substances. They dissolve only in strongly polar solvents, such as DMF, DMSO, to form solutions which slowly become colourless upon standing in air. The complexes are X-ray amorphous. Their IR spectra show a small redistribution of the intensities and a small shift of the (Mo=S) and (S–S) vibrational bands while the Mo=O valence vibrational band is practically the same in the original oxothio-complex and in the complexes III–V.

Complex III is a diamagnetic substance while IV and V are paramagnetic ones. In the case of V the paramagnetism is temperature dependent: the value of  $\mu_{\text{eff}}$  increases from 1.67 BM at 77 K to 1.84 BM at 300 K. For complex IV this value at 300 K is 3.06 BM. Such values are inconsistent with the presence of only one type of Co and Ni coordination and indicate that there are several types of metal coordination in these complexes. Complexes III–V are probably coordination polymers with the coordination of the Co, Ni, and Cu atoms occurring through the sulfur atoms of the Mo=S or S–S fragments. In the  $(\text{Ph}_4\text{P})_2\text{M}(\text{MoO}_2\text{S}_2)$  (M = Co, Ni) complexes described in ref. 19 the oxothiomallate ligand coordinates the Co and Ni atoms through sulfur atoms and not through oxygen.

In DMF solutions complexes III–V undergo solvolysis which is indicated by the relatively high values of the electrical conductivity of the solutions. Considerable dissociation of III–V is also indicated by the value of the magnetic susceptibility of V in DMF (2.43 BM at 300 K) which is consistent with the formation of the octahedral complex  $[\text{Ni}(\text{DMF})_6]^{2+}$  [20]. There are many examples of the solvolysis of complexes with an aprotic solvent with a donor number as large as that of DMF [20], but complexes of Fe, Co, Ni with  $\text{MoS}_4^{2-}$  and  $\text{WS}_4^{2-}$  usually do not dissociate in DMF. According to our

results the complexes with  $\text{Mo}_2\text{S}_7\text{O}^{2-}$  are less strong than those with  $\text{MS}_4^{2-}$ . The amorphous thio-complexes are not numerous. Among them are  $(\text{Ph}_4\text{P})_2\text{Fe}(\text{MoS}_4)_2$  [21] and also the products of the reactions of Cu(II) compounds with  $\text{MoS}_4^{2-}$  having the composition  $\text{CuMoS}_4 - x\text{O}_x$  ( $x = 2, 3$ ) [22]. The synthesis of amorphous heterometallic thio-complexes containing Cu, Ni, Co and Mo is of interest because of their potential use as catalysts [2, 5].

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