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Triangular Thiocomplexes of Molybdenum: Reactions with Halogens, Hydrohalogen Acids and Phosphines

V. P. FEDIN*, M. N. SOKOLOV, YU. V. MIRONOV, B. A. KOLESOV, S. V. TKACHEV and V. YE. FEDOROV

Institute of Inorganic Chemistry, Prospekt Lavrentyeva 3, 630090 Novosibirsk (U.S.S.R.)

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Abstract

The triangular $(NH_4)_2Mo_3S_{13}\cdot 2H_2O$ complex interacts with Cl_2 and Br_2 in CH_3CN and with concentrated hydrohalogen acids HX (X = Cl, Br and I) retaining its $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3^{4+}$ cluster fragment to produce the $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3X_6^{2-}$ complexes in high yields. IR and Raman spectra of the $Mo_3S_7X_6^{2-}$ complexes have been studied. Salts of $Mo_3S_7X_6^{2-}$ (X = Cl, Br) containing ^{92}Mo, ^{100}Mo and ^{34}S isotopes and compounds with $\mu_2\text{-}(^{32}S\text{-}^{34}S)$ ligands have been also synthesized. For $Mo_3S_7Cl_6^{2-}$, an analysis of the normal vibrations has been performed.

The $Mo_3S_7X_6^{2-}$ complexes (X = Cl, Br) interact with phosphines (PPh_3 and dppe). The reactions proceed with elimination of the $\mu_2\text{-}S_2$ sulfurs to form sulfides of the phosphines and the phosphine complexes $Mo_3S_4X_4\cdot 3PPh_3$ and $Mo_3S_4X_4\cdot 3dppe$ containing a $Mo_3S_4^{4+}$ cluster fragment. It has been shown, for the reaction of $Mo_3(\mu_3\text{-}^{34}S)(\mu_2\text{-}^{32}S_e\text{-}^{34}S_a)_3Cl_6^{2-}$ with PPh_3, that it is the equatorial $\mu_2\text{-}S_2$ sulfurs that are predominantly eliminated.

Introduction

The triangular molybdenum thiocomplex $(NH_4)_2Mo_3S_{13}\cdot 2H_2O$ (I) first prepared by Müller and coworkers exhibits an interesting structure [1, 2]. There are both terminal and bridging S_2 ligands: $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(S_2)_3^{2-}$. Being now readily available [1–3], the complex provides a useful system to study the differences in reactivity between the differently coordinated S_2 ligands. The reactions of I with KCN [4], Naedt [5], $H_2C_2O_4$ [6] and H_3NTA [6] have been studied earlier. In all of these reactions the $Mo_3S_7^{4+}$ cluster fragment is not preserved and there takes place elimination of sulfur from the $\mu_2\text{-}S_2$ ligands to yield compounds containing a $Mo_3S_4^{4+}$ cluster fragment. In the present work it has been shown that in the reactions of the Müller complex with halogens and hydrohalogen acids the $Mo_3S_7^{4+}$ cluster fragment is preserved and the $Mo_3S_7X_6^{2-}$ thiohalide complexes (X = Cl, Br, I) are produced. On the other hand, these complexes readily undergo interactions with phosphines allowing a convenient preparation of $Mo_3S_4^{4+}$ complexes in organic solvents.

Experimental

Materials and Apparatus

The $(NH_4)_2Mo_3S_{13}\cdot 2H_2O$ complex was synthesized from $Mo_3S_7X_4$ (X = Cl, Br) and ammonium polysulfide [3]. Acetonitrile was distilled over P_4O_{10}, methanol over BaO, nitrobenzene *in vacuo*. The isotope-containing systems used in this study were prepared from compounds of molybdenum metal which contained 95% of ^{92}Mo and ^{100}Mo isotopes and from sulfur containing 99.95% of ^{34}S. All other reagents were chemically pure. The reactions with phosphines were carried out using standard Schlenk technique. All other syntheses were carried out in the air. The IR spectra in the region 4000–400 cm^{-1} were obtained on a IR-75 spectrometer (Carl Zeiss, Jena) using KBr pellets and those in the 700–20 cm^{-1} region on a Fourier IFS-113 spectrometer (Bruker) in polyethylene. The Raman spectra were recorded on a DFS-24 spectrometer using the 632.8 nm line of a He–Ne laser for excitation. The accuracy of determination of the line positions was $\leqslant 1$ cm^{-1}. Molar conductivity was determined for 10^{-4} M solutions in nitrobenzene. The mass spectra were recorded on a MI-1305 spectrometer. Identification of ions was made on the basis of masses and isotope abundances. The $^{31}P\{^1H\}$ spectra were measured on a SXP-4-100 (Bruker) spectrometer at 36.45 MHz for 0.05 M solutions in CH_2Cl_2/C_6D_6 at room temperature. The chemical shifts are given relative to 85% H_3PO_4 (the external reference). Analytical data and some properties of triangular thiohalide and phosphinethiohalide complexes are shown in Table 1.

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*Author to whom correspondence should be addressed.

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TABLE 1. Analytical data and some properties of triangular thiocomplexes of molybdenum

Compound	Colour	Yield (%)	Analyses Found (calculated (%))						Some properties
			C	H	N	Mo	S	X	
$(NH_4)_2Mo_3S_7Cl_6 \cdot 2H_2O$ (II)	yellow	61		1.24 (1.26)	3.39 (3.51)	35.90 (36.11)	29.25 (28.16)		
$(Et_4N)_2Mo_3S_7Br_6$ (III)	orange	92	15.74 (15.34)	3.40 (3.22)	2.36 (2.24)	22.39 (22.99)	18.78 (17.92)	38.29 (39.15)	electronic spectrum in CH_3CN, λ (nm): 270(sh), 417(sh)
$(NH_4)_2Mo_3S_7I_6$ (IV)	dark-red	13			2.03 (2.14)		16.55 (17.09)	58.67 (58.17)	
$(Me_4N)_2Mo_3S_7Cl_6$ (V)	yellow	85	10.67 (11.00)	2.69 (2.77)	2.95 (3.21)	34.06 (32.96)	25.80 (25.70)	24.14 (24.36)	electronic spectrum in CH_3CN, λ (nm) (ϵ (M^{-1} cm^{-1})): 254 (208), 280 (142), 370(sh)
$(Et_4N)_2Mo_3S_7I_6$ (VI)	dark-red	86	12.91 (12.53)	2.65 (2.63)	1.78 (1.83)		14.68 (14.63)	50.66 (49.63)	electronic spectrum in CH_3CN, λ (nm) (ϵ (M^{-1} cm^{-1})): 240(790), 280(sh), 350(460)
$Mo_3S_4Cl_4 \cdot 3PPh_3$ (VII)	green	82	47.90 (48.21)	3.63 (3.34)			8.87 (9.51)		very instable in solutions
$Mo_3S_4Cl_4 \cdot 3dppe$ (IX)	bright green	51	52.79 (53.42)	4.29 (4.11)		17.23 (16.43)	7.41 (7.32)		electronic spectrum in CH_2Cl_2, λ (nm) (ϵ (M^{-1} cm^{-1})): 412(8300), 630(610). Λ_M: 24 ohm^{-1} cm^2 M^{-1} NMR ^{31}P: 34.9(1P), 25.1(1P)
$Mo_3S_4Br_4 \cdot 3PPh_3$ (VIII)	bright green	60	41.86 (42.60)	3.27 (3.10)		19.02 (18.87)	8.41 (8.45)		electronic spectrum in CH_2Cl_2, λ (nm) (ϵ (M^{-1} cm^{-1})): 377(7550) NMR ^{31}P: 24.1(2P), −2.6(1P)
$Mo_3S_4Br_4 \cdot 3dppe$ (X)	bright green	48	49.16 (48.49)	3.86 (3.42)		14.47 (14.92)	5.97 (6.63)		NMR ^{31}P: 33.3(1P), 19.8(1P)

Preparation of $(NH_4)_2Mo_3S_7Cl_6 \cdot 2H_2O$ (II)

The complex was obtained by passing gaseous Cl_2 through a suspension of complex **I** (0.50 g) in 50 ml of CH_3CN for 10 min at a Cl_2 flow rate of about 100 ml/min. The precipitated solid was filtered off, washed with methylene chloride and dried under vacuum.

Preparation of $(Et_4N)_2Mo_3S_7Br_6$ (III)

A suspension of complex **I** (0.50 g) in 50 ml of CH_3CN to which 1 ml Br_2 and 1.0 g Et_4NBr were added was boiled for 5 min. The solution was filtered, cooled down and then 30 ml ether was added. After an overnight standing the precipitated solid was filtered off, washed with alcohol, methylene chloride and dried under vacuum.

Interaction of I with HX (X = Cl, Br, I) (General Procedure)

Complex **I** (0.50 g) was boiled in 50 ml of concentrated acids for 15–20 min and the solution filtered while hot. A solid precipitated upon cooling only in the reaction with HI (complex **IV**). Adding Me_4NCl (1.0 g) or Et_4NBr to the solution afforded precipitation of complexes **III**, **V** and **VI**.

Analogously, by adding PPh_4Cl and PPh_4Br to hot solutions in HCl and HBr, the $(PPh_4)_2Mo_3S_7Cl_6$ and $(PPh_4)_2Mo_3S_7Br$ salts were obtained in a 80–85% yield.

Preparation of $Mo_3S_4Cl_4{\cdot}3PPh_3$ (VII) and $Mo_3S_4Br_4{\cdot}3PPh_3$ (VIII)

A suspension of $(R_4N)_2Mo_3S_7X_6$ (1.00 g) (R = Me, Et; X = Cl, Br) and PPh_3 (2.00 g) in methanol (50 ml) was stirred for 1 h. The precipitated green solid was filtered off, washed with hot methanol and benzene and dried under vacuum.

Preparation of $Mo_3S_4Cl_4{\cdot}3dppe$ (IX) and $Mo_3S_4Br_4{\cdot}3dppe$ (X)

$(R_4N)_2Mo_3S_7X_6$ (1.0 g) (R = Me, Et; X = Cl, Br) and dppe (2.0 g) in methanol (50 ml) were boiled for 1 h. The bright green precipitate was recrystallized from a CH_2Cl_2/hexane mixture.

Results and Discussion

Preparation and Properties of the $Mo_3S_7X_6^{2-}$ salts (X = Cl, Br, I)

The $(NH_4)_2Mo_3S_{13}$ complex (**I**) provides a convenient starting material for the synthesis of triangular thiohalide complexes of molybdenum $Mo_3S_7X_6^{2-}$ (X = Cl, Br, I). We have found that **I** interacts with Cl_2 and Br_2 and does not interact with I_2 in acetonitrile. The reaction with chlorine proceeds rapidly at room temperature and is accompanied by heat evolution. To rapidly bring to completion the reaction with bromine the reaction mixture must be boiled. Thus, the easiness of the interaction with **I** decreases in the series $Cl_2 > Br_2 \gg I_2$.

The completion of the reaction with Cl_2 is easily observable visually by conversion of the red precipitate to the yellow precipitate of the $(NH_4)_2Mo_3S_7Cl_6{\cdot}2H_2O$ salt (**II**). The thiobromide complex has been isolated as the Et_4N^+ salt **III** (eqn. (2)).

$$\underset{\textbf{I}}{(NH_4)_2Mo_3S_{13}{\cdot}2H_2O} \xrightarrow{Cl_2} \underset{\textbf{II}}{(NH_4)_2Mo_3S_7Cl_6{\cdot}2H_2O} \qquad (1)$$

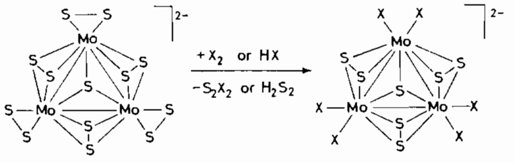
$$\underset{\textbf{I}}{(NH_4)_2Mo_3S_{13}{\cdot}2H_2O} \xrightarrow[Et_4NBr]{Br_2} \underset{\textbf{III}}{(Et_4N)_2Mo_3S_7Br_6} \qquad (2)$$

The triangular molybdenum thiohalide complexes are best obtained by reactions of **I** with concentrated hydrohalogen acids HX (X = Cl, Br, I). We have found that **I** interacts with concentrated HX to form dark red solutions. The ammonium salts of $Mo_3S_7X_6^{2-}$ are markedly soluble in acids and only $(NH_4)_2Mo_3S_7I_6$ (**IV**) crystallizes from the solution in a low yield. However, by adding Me_4NX, Et_4NX or PPh_4X it is possible to obtain high yields of the corresponding salts. Examples of such salts **IV**–**VI** are shown in Table 1. The yields of alkylammonium or phosphonium salts are 85–95%.

Müller and co-workers obtained in 1986 a 3% yield of $(Et_4N)_3(Mo_3S_7Cl_7){\cdot}CH_2Cl_2$ in the reaction of $MoCl_5$ and NaSH in methylene chloride [7]. We have reported the synthesis of $(PPh_4)_2Mo_3S_7X_6$ salts (X = Cl, Br) which were obtained by heating polymeric $Mo_3S_7X_4$ complexes in a PPh_4X melt [8]. This procedure gave a 75% yield of the thiochloride salt. The thiobromide salt, being thermally less stable, formed only in a 37% yield.

The structure of $(PPh_4)_2(Mo_3S_7Cl_6)$ has been established by X-ray diffraction analysis [9]. The $Mo_3S_7X_6^{2-}$ complexes show very characteristic vibrational spectra at 600–100 cm^{-1}. A comparison of the vibrational spectra of complexes **II**–**VI** obtained in the present work with those of $(PPh_4)_2Mo_3S_7X_6$ (X = Cl, Br) and polymeric $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3X_2X_{4/2}$ complexes (X = Cl, Br) [10–12] allowed us to conclude that they all have an $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)X_6^{2-}$ fragment.

Thus in the interaction of **I** with halogens or acids the $Mo_3S_7^{4+}$ cluster fragment is preserved, the formal result of the reaction being nucleophilic substitution of the terminal disulfide ligands by halide ions.



(3)

Noteworthy is a very large difference between the reactivities of the S_2 ligands in the Müller complex. The terminal ligands are replaced by the halide ligands whereas the $\mu_2\text{-}S_2$ ligands were preserved under very forcing conditions such as boiling with 10 to 100 equivalents of Br_2 in CH_3CN or a prolonged boiling in concentrated HX acids.

Let us note also that the easiness of the interaction of **I** with the acids decreases in the series HI > HBr > HCl. The interaction of **I** with hydrofluoric acid produces thiomolybdenic acid **XI** (eqn. (4)) and not the thiofluoride complex

$$\underset{\textbf{I}}{(NH_4)_2Mo_3S_{13}{\cdot}2H_2O} \xrightarrow{HF\ +\ H_2O} \underset{\textbf{XI}}{H_2Mo_3S_{13}{\cdot}2H_2O} \qquad (4)$$

Complex **XI** is not soluble in HF. It is an X-ray amorphous material and its IR spectrum fully coincides with that of **I**, except for ν_{NH} of the NH_4^+ cation.

Vibrational Spectra of $Mo_3S_7X_6^{2-}$ (X = Cl, Br, I)

The IR and Raman spectra of the triangular molybdenum thiohalide complexes are shown in Fig. 1. Along with the samples with natural isotope

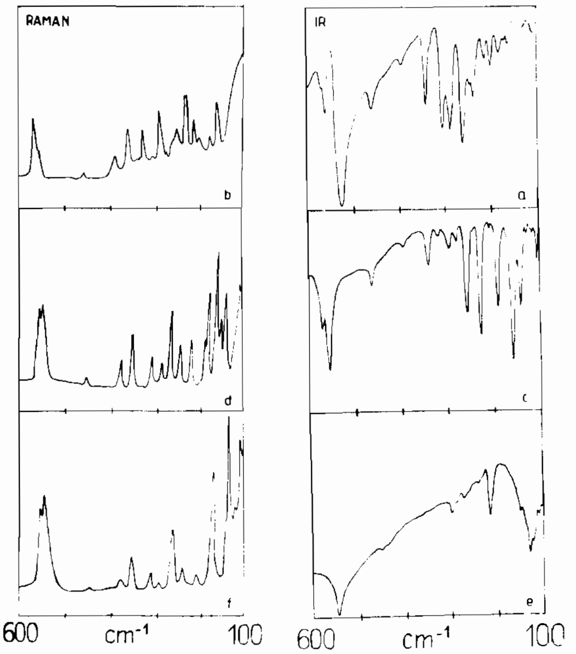


Fig. 1. IR (in polyethylene) and Raman spectra of trinuclear thiohalide complexes of molybdenum: $(PPh_4)_2Mo_3S_7Cl_6$ (a) and (b); $(Et_4N)_2Mo_3S_7Br_6$ (c) and (d); $(Et_4N)_2Mo_3S_7I_6$ (e) and (f).

contents the IR and Raman spectra have been also taken for ^{92}Mo, ^{100}Mo and ^{34}S containing compounds. The following complexes have been studied: $(PPh_4)_2{}^{92}Mo_3S_7Cl_6$ (**XIIa**), $(PPh_4)_2{}^{100}Mo_3S_7Cl_6$ (**XIIb**), $(PPh_4)_2Mo_3{}^{34}S_7Cl_6$ (**XIIc**), $(PPh_4)_2Mo_3(\mu_3\text{-}{}^{34}S)(\mu_2\text{-}{}^{32}S_e\text{-}{}^{34}S_a)_3Cl_6$ (**XIId**), $(Et_4N)_2Mo_3{}^{34}S_7Br_6$ (**IIIa**), $(Et_4N)_2Mo_3(\mu_3\text{-}{}^{34}S)(\mu_2\text{-}{}^{32}S_e\text{-}{}^{34}S_a)_3Br_6$ (**IIIb**), $(Et_4N)_2Mo_3(\mu_3\text{-}{}^{32}S)(\mu_2\text{-}{}^{34}S_e\text{-}{}^{32}S_a)_3Br_6$ (**IIIc**).

Let us note the following important feature of the structure of $Mo_3S_7X_6^{2-}$ [9]: the non-equivalence of the sulfurs of the μ_2-S_2 ligands. Three of them practically lie in the Mo_3 plane (equatorial, S_e, atoms) with the other three occupying the side of the Mo_3 triangle opposite to μ_3-S (axial, S_a, atoms).

The Müller complex has an analogous arrangement of its μ_2-S_2 ligands [1,2] and it is this asymmetry that makes possible preparation of complexes **Ia** and **Ib** (eqns. (5) and (6)) (the synthesis of such complexes will be described elsewhere).

$$Mo_3S_7Br_4 \xrightarrow{{}^{34}S_x{}^{2-}} Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_e\text{-}{}^{34}S_a)_3({}^{34}S_2)_3{}^{2-} \tag{5}$$

Ia

$$Mo_3{}^{34}S_7Br_4 \xrightarrow{S_x{}^{2-}} Mo_3(\mu_3\text{-}{}^{34}S)(\mu_2\text{-}{}^{34}S_e\text{-}S_a)_3(S_2)_3{}^{2-} \tag{6}$$

Ib

Complexes **IIIb**, **IIIc** and **XIId** were obtained from **Ia** and **Ib**.

We have performed a calculation of the vibrational spectra for $Mo_3S_7Cl_6{}^{2-}$ using programs taken from ref. 13 and a zero approximation of the force constants taken from ref. 12. The vibrational (IR and Raman) frequencies for $Mo_3S_7Cl_6{}^{2-}$ and the shift values upon the $^{92}Mo \rightarrow {}^{100}Mo$ and $^{32}S \rightarrow {}^{34}S$ isotope transitions have been used as the experimental basis for these calculations. The low frequency (<250 cm^{-1}) internal vibrations of $Mo_3S_7Cl_6{}^{2-}$ relating mainly to deformations are strongly mixed with external vibrations – translations and librations. The main attention in the calculations has been given, therefore, to the internal valence vibrations. This approximation is reasonable for all bonds except for Mo–Mo. The vibrational frequencies of this bond fall in the 170–200 cm^{-1} region which makes the force constant found for this bond the least certain of the whole set of force constants. The final variant is given in Table 2. Table 3 shows the experimental and calculated vibrational frequencies for $Mo_3S_7Cl_6{}^{2-}$ salts and their shifts upon isotope substitutions. In Table 4 the vibrational modes are shown as distributions of their potential vibrational energies among the groups of equivalent vibrational coordinates.

From Table 4 it can be seen that corresponding to the 560 and 568 cm^{-1} frequencies are the valence vibrations of μ_2-S_2. On going from the μ_2-(^{32}S-^{32}S)

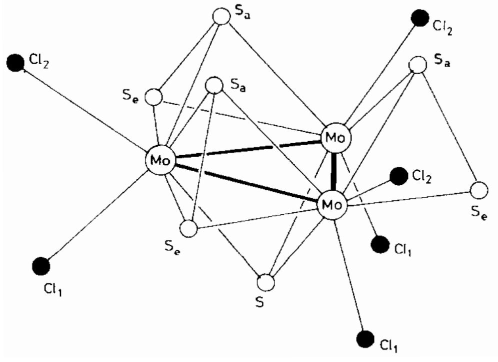


TABLE 2. Bond force constants in $Mo_3S_7Cl_6{}^{2-}$

Bonds	Force constants (mdyn/Å)
Mo–Mo	1.2
Mo–μ_3-S	1.8
Mo–μ_2-S_e	1.5
Mo–μ_2-S_a	1.7
Mo–Cl_1	1.7
Mo–Cl_2	1.4
S_a–S_e	2.4

TABLE 3. Experimental and calculated vibrational frequencies of tetraphenylphosphonium salts of $Mo_3S_7Cl_6^{2-}$ and their shifts upon isotope substitution[a]

ν_{exp} (cm^{-1})	ν_{calc} (cm^{-1})	$\Delta\nu$ (cm^{-1})					
		XIIa → XIIb		XII → XIIc		XII → XIId	
		exp.	calc.	exp.	calc.	exp.	calc.
183 IR	182	3	2.8	1	0.7	0	0.4
261 IR	259			4	3.1	3	2.0
277 Raman	268	?	0.2	?	5.0	?	2.2
290 IR, Raman	284	1	0.1	6	6.8	3	4.4
305 IR	304	2	2.2	0	1.1	0	2.8
305 IR	307	2	0.6	6	6.6	5	2.7
332 IR, Raman	332	4	2.7	4	6.8	2	1.7
342 IR	342	6	4.1	5	4.8	5	3.9
363 IR, Raman	362	8	7.1	5	3.8	3	2.2
392 IR, Raman	392	6	6.4	4	4.4	3	2.0
461 IR, Raman	461	6	6.4	9	7.8	9	7.6
560 IR, Raman	560	1	1.4	17	15.5	8	7.3
568 IR, Raman	566	1	1.2	16	15.7	8	6.8

[a] $(PPh_4)_2Mo_3S_7Cl_6$ (XII); $(PPh_4)_2{}^{92}Mo_3S_7Cl_6$ (XIIa); $(PPh_4)_2{}^{100}Mo_3S_7Cl_6$ (XIIb); $(PPh_4)_2Mo_3{}^{34}S_7Cl_6$ (XIIc); $(PPh_4)_2Mo_3(\mu_3\text{-}{}^{34}S)(\mu_2\text{-}{}^{32}S_e\text{-}{}^{34}S_a)_3Cl_6$ (XIId).

TABLE 4. Distribution of the potential energy among the groups of equivalent vibrational coordinates of the $Mo_3S_7Cl_6^{2-}$ complex

ν (cm^{-1})	Type of vibration	Distribution of the potential energy (%)						
		Mo–Mo	Mo–μ_3-S	Mo–μ_2-S_e	Mo–μ_2-S_a	Mo–Cl_1	Mo–Cl_2	S_a–S_e
182	A_1	70	1	0	4	7	18	0
259	E_g	0	27	0	21	16	35	1
268	E	0	18	11	38	19	13	1
284	A_1	0	0	43	15	22	0	18
304	A_1	8	15	0	3	3	71	0
307	A_1	1	7	37	12	42	0	1
332	E	0	1	8	58	27	1	5
342	E	0	22	46	2	0	25	4
362	E	11	9	23	14	10	15	18
392	E	0	15	11	40	27	6	1
461	A_1	9	77	0	0	1	10	2
560	E	0	0	13	16	0	0	70
566	A_1	1	0	9	22	1	0	67

complex to the complex with μ_2-(^{34}S-^{34}S) the isotope shift reaches almost the highest possible value, namely 17.2 cm^{-1}. On going from the complex with μ_2-(^{32}S-^{32}S) to the complex with μ_2(^{32}S-^{34}S) the isotopic shift is 8 cm^{-1} (the highest possible value is 8.4 cm^{-1}). The force constant of the S–S bond in $Mo_3S_7Cl_6^{2-}$ is 2.4 mdyn/Å which is closer to the value of $f_{S_2^{2-}} = 1.9$ mdyn/Å than to $f_{S_2^{\cdot -}} = 3.3$ mdyn/Å.

The 461 cm^{-1} frequency is one of the most characteristic frequencies in the IR and Raman spectra and belongs to vibrations involving μ_3-S. The force constant of the Mo–μ_3-S bonds exceeds somewhat those of the Mo–μ_2-S bonds. The vibrational frequencies of the Mo–S bonds are strongly mixed with those of the Mo–Cl bonds due to similarity of the atomic masses and force constants. For the $Mo_3S_7X_6^{2-}$ (X = Br, I) complexes the analysis of the normal vibrations was not performed because of the lack of structural data for these compounds. Table 5 shows IR frequencies for the $Mo_3S_7Br_6^{2-}$ complex together with the values of the shifts upon isotope exchange. A comparison of the vibrational frequencies in the vibrational spectra (X = Cl, Br, I) as well as of the shifts in these frequencies upon isotope exchange (Tables 3 and 5) allows the 570–

TABLE 5. Experimental vibrational frequencies in the IR spectra of the $(Et_4N)_2Mo_3S_7Br_6$ complex and their shifts upon isotope exchange[a]

III ν (cm^{-1})	III → IIIa $\Delta\nu$ (cm^{-1})	III → IIIb $\Delta\nu$ (cm^{-1})	III → IIIc $\Delta\nu$ (cm^{-1})
567	17	8	7
553	16	8	7
464	8	8	0
391	2	3	2
340	7	7	3
317	7	4	5
296	10	6	8
274	1	0	1
252	0	0	0
225	5	1	2
189	3	1	1
162	5	3	4
144	3	1	1
109	2	2	1

[a] $(Et_4N)_2Mo_3S_7Br_6$ (III), $(Et_4N)_2Mo_3{}^{34}S_7Br_6$ (IIIa), $(Et_4N)_2Mo_3(\mu_3\text{-}{}^{34}S)(\mu_2\text{-}{}^{32}S_e\text{-}{}^{34}S_a)_3Br_6$ (IIIb), $(Et_4N)_2Mo_3(\mu_3\text{-}{}^{32}S)(\mu_2\text{-}{}^{34}S_e\text{-}{}^{32}S_a)_3Br_6$ (IIIc).

540 vibrations to be reliably assigned to the S_2 valence vibrations. The weak bands at 465–445 cm^{-1} belong to vibrations involving μ_3-S.

In the thiochloride complex $Mo_3S_7Cl_6{}^{2-}$ there is a series of intense bands at 340–260 cm^{-1} having an essential contribution from vibrations involving chlorine atoms. These intense bands are absent in the thiobromide and thioiodide complexes. In the thiobromide complex there appears a series of intense bands at 260–160 cm^{-1} and in the iodide complex it is the bands at about 140 cm^{-1} that are strong. These vibrations appear to have a considerable contribution from vibrations involving halogen atoms.

Reactions of $Mo_3S_7X_6{}^{2-}$ with Phosphines. Synthesis of $Mo_3S_4{}^{4+}$ Phosphine Thiohalide Complexes

The $Mo_3S_7X_6{}^{2-}$ complexes are now readily available which allows us to study their chemical properties. Interaction of phosphines (PPh_3, dppe) with $(Me_4N)_2Mo_3S_7Cl_6$ or $(Et_4N)_2Mo_3S_7Br_6$ in methanol was found by us to produce complexes VII–X (eqns. (7) and (8))

$$(R_4N)_2Mo_3S_7X_6 + 6PPh_3 \longrightarrow Mo_3S_4X_4\cdot 3PPh_3 + 3SPPh_3 + 2R_4NX \qquad (7)$$

X = Cl (VII), Br (VIII)

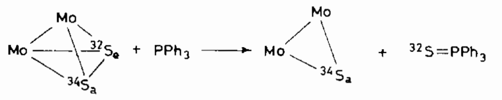
$$(R_4N)_2Mo_3S_7X_6 + 4.5\text{dppe} \longrightarrow Mo_3S_4X_4\cdot 3\text{dppe} + 1.5\text{dppeS}_2 + 2R_4NX \qquad (8)$$

X = Cl (IX), Br (X)

In these reactions, under the action of nucleophiles, elimination of one of the sulfurs of the μ_2-S_2 ligands takes place to produce sulfides of the phosphines. These products have been isolated from the reaction mixture in a practically quantitative yield (eqn. (9)).

(9)

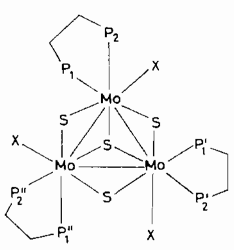
Since the μ_2-S_2 ligands are coordinated asymmetrically relative the Mo_3 triangle one could expect preferential elimination of either equatorial or axial sulfurs. The stereochemistry of sulfur elimination has been studied using isotope-containing compounds. Triphenylphosphine sulfide formed in the reaction of PPh_3 with $(Et_4N)_2Mo_3(\mu_3\text{-}{}^{34}S)(\mu_2\text{-}{}^{32}S_e\text{-}{}^{34}S_a)_3Br_6$ (**IIIb**) contained, according to mass spectral data, over 80% of $^{32}SPPh_3$. Thus, the elimination of sulfur under the action of phosphines proceeds with a rather high selectivity and it is the equatorial sulfurs that are chiefly eliminated (eqn. (10)).



(10)

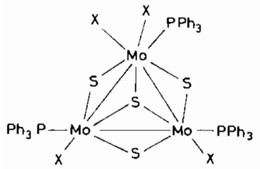
Analysis of the literature shows that the synthesis of $Mo_3S_4{}^{4+}$ complexes in aqueous solutions is, on the whole, well developed [14–16] but the work on the synthesis in organic solvents has been started only recently [17, 18]. Saito and co-workers have obtained $Mo_3S_4Cl_4(PEt_3)_3\cdot 2MeOH$ and $Mo_4S_4Cl_4(PEt_3)_4\cdot MeOH$ by interacting PEt_3 with polymeric $Mo_3S_7Cl_4$ [17]. Cotton and Llusar have obtained $[Mo_3S_4Cl_3(dmpe)_3]PF_6\cdot MeOH$ by reacting NaSH and NH_4PF_6 with mononuclear $MoCl_3\cdot 3THF$ [18]. Attempts to employ other phosphines (dmpm or monodentate ones) give different products [18]. The reaction of $Mo_3S_7X_6{}^{2-}$ with PPh_3 and dppe studied by us extends the number of $Mo_3S_4{}^{4+}$-containing phosphine complexes.

Compounds VII–X are green crystals readily soluble in CH_2Cl_2, CH_3CN, the solutions of VII and VIII undergoing rapid decomposition. The characteristic electronic absorption spectra in the visible region indicate the presence of chromophore $Mo_3S_4{}^{4+}$ [14]. Complexes IX and X are 1:1 electrolytes in nitrobenzene. We expect that the structure of the $Mo_3S_4(dppe)_3X_3{}^+$ cation is analogous to that of the $Mo_3S_4(dmpe)_3Cl_3{}^+$ cation [18].



The μ_3-S, P_1 and X atoms lie on one side of the Mo_3 triangle, with the μ_2-S and P_2 atoms occupying the opposite side. In other words, the P_1 and X atoms are *trans* to μ_2-S and the P_2 atoms are *trans* to μ_3-S. This leads to two fully symmetrical signals in the $^{31}P\{^1H\}$ NMR spectra of complexes **IX** and **X** in solutions (Fig. 2). The fine structure of the spectrum is due to magnetic non-equivalence of the molybdenum atoms.

For the complexes with PPh_3 we propose the following structure:



In the $^{31}P\{^1H\}$ NMR spectra there are two signals with an integral intensity 2:1. The bulky PPh_3 ligand prevents coordination of the solvent molecules and, in contrast to the $Mo_3S_4Cl_4(PEt_3)_4(MeOH)$ and $Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2$ complexes [17], complexes **VII** and **VIII** are coordinatively unsaturated compounds. This predetermines instability of these complexes in solutions, for example, on account of formation of coordination polymers with halide bridges.

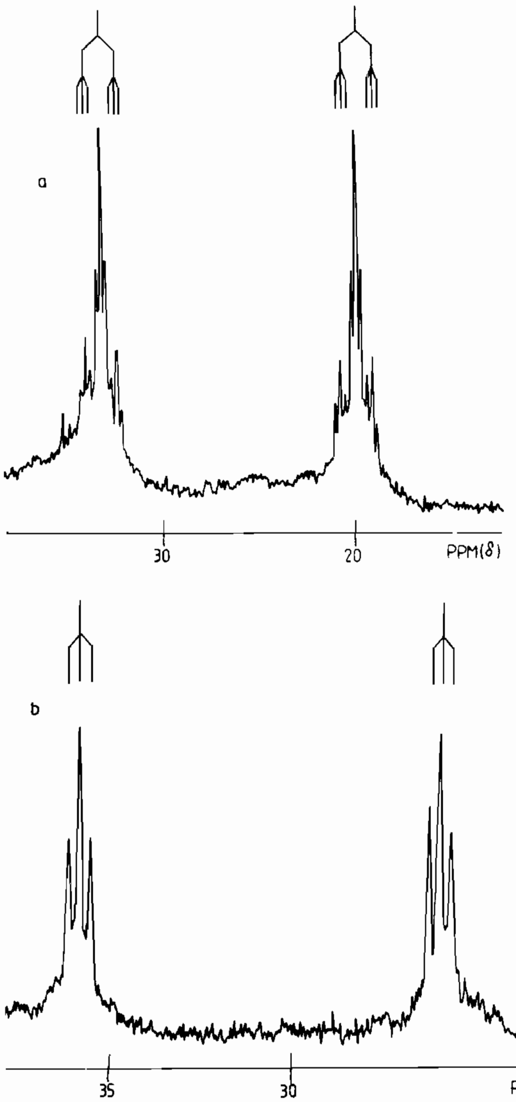


Fig. 2. $^{31}P\{^1H\}$ NMR spectra of $Mo_3S_4Br_4 \cdot 3dppe$ (a) and $Mo_3S_4Cl_4 \cdot 3dppe$ (b) in CH_2Cl_2/C_6D_6 at 25 °C.

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