Reactions of triangular $Mo_3S_7X_6^{2-}$ (X = Cl, Br, NCS) complexes with KSCN and KSeCN, resulting in stereoselective substitution of sulfur atom in asymmetrically coordinated μ_2-S_2 ligand. X-ray structure of $(PPN)_2Mo_3(\mu_3\text{-}S)(\mu_2\text{-}SSe)_3Cl_6$

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Abstract

The $Mo_3S_7X_6^{2-}$ salts (X = Cl, Br, NCS) interact with KSeCN at room temperature in CH_3CN to form KSCN and $Mo_3S_4Se_3(NCS)_6^{2-}$. The stereochemistry of this reaction has been studied and it was shown that substitution only occurs at the equatorial sulfur atoms of the μ_2-S_2 ligand. By treating $(Et_4N)_2Mo_3S_4Se_3(NCS)_6$ with conc. HCl $(Et_4N)_2Mo_3S_4Se_3Cl_6$ was prepared from which $(PPN)_2Mo_3S_4Se_3Cl_6$ (**IIIb**) was obtained by the exchange of the cation. The structure of the latter was established by X-ray structural analysis. The crystals of **IIIb** are triclinic, space group $P1$, $a = 13.650$ (2), $b = 18.159(3)$, $c = 19.009(3)$ Å; $\alpha = 99.48(1)$, $\beta = 109.23(1)$, $\gamma = 109.32(1)$°, $Z = 2$. With a total number of independent reflections of 7937, the structure has been solved to $R = 0.054$ ($R_w = 0.077$). The selenium atoms lie essentially in the plane of the isosceles Mo_3 triangle. The S–Se distances are 2.156(5)–2.166(3) Å; Mo–Mo distances are 2.765(2)–2.787(2) Å. The equatorial sulfur of the μ_2-S_2 group was found to undergo isotopic exchange with the thiocyanate sulfur. The interaction of $(Et_4N)_2Mo_3{}^{34}S_7Cl_6$ with KSCN afforded, according to the vibrational spectroscopy data, $(Et_4N)_2Mo_3(\mu_3\text{-}^{34}S)(\mu_2\text{-}^{32}S^{34}S)_3(NCS)_6$.

Introduction

Complexes with polychalcogenide ligands have been intensively studied recently with increasing emphasis on the polyselenide and polytelluride complexes [1, 2]. However, the potentially very rich area of mixed polychalcogenides with S–Se, Se–Te or S–Te bonds still remains only a very small part of these studies [3, 4]. The study of the reactivity of polychalcogenide ligands is also only in its early stages [5–8].

We have shown, in the course of our studies of $Mo_3S_7^{4+}$ complexes, that the sulfur atoms of the asymmetrical μ_2-S_aS_e ligand may show different reactivities (a and e are the axial and equatorial positions with respect to the Mo_3 triangle).

Thus, under the action of $(NH_4)_2{}^{34}S_x$ on $Mo_3S_7Br_4$ isotopic exchange in the $Mo_3S_7^{4+}$ core [9] takes place (eqn. (1))

$$Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_aS_e)_3^{4+} + {}^{34}S_x^{2-} \longrightarrow Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_a{}^{34}S_e)_3^{4+} + S_x^{2-} \quad (1)$$

where substitution only occurs on the equatorial atoms.

With Ph_3PSe the same sulfur atoms were substituted by selenium. In this way we were able to obtain for the first time complexes of the μ_2-S_aSe_e ligand $M_3(\mu_3\text{-}S)(\mu_2\text{-}SSe)_3X_6^{2-}$ (M = Mo, W; X = Cl, Br). For the $(Ph_3PEt)_2Mo_3S_4Se_3Cl_6$ salt the crystal structure has been determined by the X-ray structural method [10].

In the present paper we report the reactions of KSeCN with $Mo_3S_7X_6^{2-}$ (X = Cl, Br, NCS) which resulted in the isolation of $Mo_3S_4Se_3(NCS)_6^{2-}$. The reaction of $Mo_3{}^{34}S_7Cl_6^{2-}$ with KSCN also proceeded with isotopic exchange and gave rise to $Mo_3{}^{34}S_4S_3(NCS)_6^{2-}$.

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Experimental

All reactions, unless otherwise stated, were carried out in air. CH_3CN was distilled over P_4O_{10}. The $Mo_3S_7X_6{}^{2-}$ salts were synthesized according to ref. 11. KSeCN was prepared by melting together $K_4Fe(CN)_6$ and Se at 250 °C with subsequent extraction with acetone [12]. $(Et_4N)_2Mo_3S_4Se_3Cl_6$ and Ph_3PSe were obtained according to ref. 10. All other reagents were commercial grade.

Determination of C, H and N were performed in the laboratory of microanalysis of the Institute of Organic Chemistry (Novosibirsk). Mo, S and Se were determined gravimetrically as $Mo(C_9H_6NO)_2$, $BaSO_4$ and Se, respectively. The IR spectra were recorded on the Fourier spectrometer IFS-113 (Bruker) in polyethylene. The Raman spectra were obtained on the DFS-24 spectrometer using the 632.8 nm line of a He–Ne lazer for the excitation.

X-ray structural analysis

The crystals of $C_{72}H_{60}Cl_6Mo_3N_2P_4S_4Se_3$ are triclinic, at 20 °C $a=13.650(2)$, $b=18.159(3)$, $c=19.009(3)$ Å, $\alpha=99.48(1)$, $\beta=109.23(1)$, $\gamma=109.32(1)°$, $Z=2$, space group $P1$. The parameters and intensities of a total of 7937 reflections were measured on the autodiffractometer Hilger-Watts (Mo Kα, graphite monochromator, $\theta/2\theta$ scanning, $\theta \leqslant 52°$). To solve and refine the structure 6871 reflections with $I \geqslant 4\sigma$ of this total amount were used. The structure has been solved by the direct method and refined by means of a full matrix least-squares procedure in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were placed in the calculated positions and refined. The final values of the divergence factors are $R=0.054$ and $R_w=0.077$. All calculations were performed on the personal computer IBM PC AT using the programms of Sheldrick [13].

Preparation of $(Et_4N)_2Mo_3S_4Se_3(NCS)_6$ (I)

From $(Et_4N)_2Mo_3S_7X_6$ (X=Cl, Br), KSeCN and KSCN

A suspension of $(Et_4N)_2Mo_3S_7Br_6$ (0.50 g, 0.40 mmol) and KSeCN (0.18 g, 1.20 mmol) in 30 ml of CH_3CN was stirred for 2 h, then 1 g KSCN was added and the stirring was continued for another 2 h. The resulting solution was filtered and evaporated, the solid was washed with water, ethanol and ether and dried *in vacuo*. Obtained 0.37 g of dark-orange powder. Yield 70%.

Anal. Calc. for $C_{22}H_{40}N_8S_{10}Se_3Mo_3$: C, 20.92; N, 8.87; H, 3.17; S, 25.44; Se, 18.78; Mo, 22.82. Found: C, 19.08; N, 8.21; H, 2.98; S, 24.80; Se, 18.81; Mo, 23.16%.

I was obtained from $(Et_4N)_2Mo_3S_7Cl_6$ by an analogous procedure, 66% yield.

From $(Et_4N)_2Mo_3S_7(NCS)_6$ and KSeCN

$(Et_4N)_2Mo_3S_7(NCS)_6$ (0.20 g, 0.18 mmol) and KSeCN (0.08 g, 0.55 mmol) in 20 ml of CH_3CN were stirred for 12 h. The solution was evaporated, the dry residual extracted with water. Evaporation of this extract gave 0.05 g KSCN (quantitative yield, identified by IR). After rinsing with water the solid was washed with alcohol and ether and dried *in vacuo*. The solid was I according to the vibrational spectroscopy and analysis. Obtained 0.12 g of I. Yield 55%.

From $(Et_4N)_2Mo_3S_7(NCS)_6$ and Ph_3PSe

A suspension of $(Et_4N)_2Mo_3S_7(NCS)_6$ (0.20 g, 0.18 mmol) and Ph_3PSe (0.18 g, 0.05 mmol) in 20 ml of CH_3CN was stirred for 2 h at room temperature. The solution was evaporated, the solid washed with hot benzene and re-precipitated with alcohol from an acetonitrile solution for purification. Obtained 0.10 g of I. Yield 53%.

From $(Et_4N)_2Mo_3S_4Se_3Cl_6$ and KSCN

$(Et_4N)_2Mo_3S_4Se_3Cl_6$ (0.25 g, 0.23 mmol) and KSCN (1.0 g, 10 mmol) in 20 ml of CH_3CN were stirred for 12 h at room temperature, filtered of KSCN and KCl, then the filtrate was evaporated and the solid re-precipitated with alcohol from CH_3CN. Obtained 0.16 g of I. Yield 55%.

Preparation of $(Et_4N)_2Mo_3S_7(NCS)_6$ (IIa)

0.40 g of $(Et_4N)_2Mo_3S_7Cl_6$ and 0.40 g of KSCN in 30 ml of CH_3CN were boiled for 2 h, then cooled down to −10 °C. The precipitated solid was filtered off, washed with water, alcohol and ether. Obtained 0.39 g of orange powder. Yield 87%.

Anal. Calc. for $C_{22}H_{40}N_8S_{13}Mo_3$: C, 23.57; H, 3.57; N, 10.00; S, 37.14; Br, 0.00. Found: C, 23.33; H, 3.60; N, 9.84; S, 37.44; Br, 0.00%.

Analogously, $(Et_4N)_2Mo_3{}^{34}S_4{}^{32}S_3(NCS)_6$ was obtained from $(Et_4N)_2Mo_3{}^{34}S_7Cl_6$ and KSCN. This reaction takes place both at room temperature and in boiling CH_3CN.

Reaction of I with HCl

0.05 g of I was boiled in 10 ml of the C_2H_5OH/HCl_{conc} mixture (1:1) for 30 min. The solution was filtered and evaporated until the onset of crystallization. Obtained 0.03 g of $(Et_4N)_2Mo_3S_4Se_3Cl_6$ (**IIIa**) (identified by vibrational spectroscopy [10]). Yield 68%.

Treatment of **IIIa** in HCl with PPNCl yields **IIIb** as a light-brown precipitate. Single crystals of **IIIb** were obtained by the diffusion of ether vapors into an acetonitrile solution of the complex.

Preparation of $(Et_4N)_5W_3S_4(NCS)_9$ (IV)

A mixture of $(Et_4N)_2W_3S_7Br_6$ [14] (0.61 g, 0.46 mmol) and KSCN (1.6 g, 16.3 mmol) in 30 ml of acetonitrile was boiled for 1 h in argon. The resulting green solution was dropped into a solution of Et_4NBr (3 g) in 100 ml H_2O. The copious precipitate was filtered and washed with water, ethanol, benzene and ether. Obtained 0.73 g of green powder. Yield 97%. IR and Raman spectra are identical to those described in ref. 14.

Anal. Calc. for $C_{49}H_{100}N_{14}W_3S_{13}$: W, 29.8. Found: W, 30.1%.

Preparation of $(Et_4N)_2W_3S_7(NCS)_6$ (V)

A mixture of $(Et_4N)_2W_3S_7Br_6$ (0.64 g, 0.49 mmol) and KSCN (1.40 g, 14.3 mmol) was stirred for 4 h at room temperature. The resulting brown precipitate was filtered and washed with water, ethanol and ether. Obtained 0.49 g. Yield 71%.

Anal. Calc. for $C_{22}H_{40}N_8S_{13}W_3$: C, 19.08; H, 2.89; N, 8.65; W, 39.88. Found: C, 18.84; H, 2.71; N, 8.65; W, 40.18%.

Results and discussion

The reaction with KSeCN

In pursuing our search for reagents capable of selectively substituting the chalcogen in the asymmetrically coordinated μ_2-S_2 ligand our attention was attracted by the pseudohalides NCX^- (X = S, Se). So far, in inorganic chemistry, these compounds have been acting primarily as ligands although it is possible to use them as a chalcogen source in organic substitution reactions [15].

The exchange occurs already at room temperature and gives rise to a complex with the μ_2-SSe ligand

TABLE 1. Bond lengths in anion (Å)

Mo(1)–Mo(2)	2.765(2)	Mo(1)–Mo(3)	2.787(2)
Mo(1)–Se(1)	2.601(3)	Mo(1)–Se(3)	2.606(2)
Mo(1)–Cl(11)	2.489(6)	Mo(1)–Cl(12)	2.453(4)
Mo(1)–S(1)	2.404(3)	Mo(1)–S(3)	2.408(5)
Mo(1)–S(4)	2.349(5)	Mo(2)–Mo(3)	2.784(2)
Mo(2)–Se(1)	2.608(3)	Mo(2)–Se(2)	2.611(3)
Mo(2)–Cl(21)	2.432(6)	Mo(2)–Cl(22)	2.492(4)
Mo(2)–S(1)	2.405(5)	Mo(2)–S(2)	2.406(5)
Mo(2)–S(4)	2.362(3)	Mo(3)–Se(2)	2.624(3)
Mo(3)–Se(3)	2.619(3)	Mo(3)–Cl(31)	2.456(4)
Mo(3)–Cl(32)	2.524(5)	Mo(3)–S(2)	2.412(3)
Mo(3)–S(3)	2.408(5)	Mo(3)–S(4)	2.354(5)
Se(1)–S(1)	2.156(5)	Se(2)–S(2)	2.162(5)
Se(3)–S(3)	2.166(3)		

TABLE 2. Bond angles in anion (°)

Mo(2)–Mo(1)–Mo(3)	60.2(1)	Mo(2)–Mo(1)–Se(1)	58.1(1)
Mo(3)–Mo(1)–Se(1)	118.2(1)	Mo(2)–Mo(1)–Se(3)	118.0(1)
Mo(3)–Mo(1)–Se(3)	58.0(1)	Se(1)–Mo(1)–Se(3)	173.7(1)
Mo(2)–Mo(1)–Cl(11)	138.5(1)	Mo(3)–Mo(1)–Cl(11)	137.8(1)
Se(1)–Mo(1)–Cl(11)	92.6(1)	Se(3)–Mo(1)–Cl(11)	93.2(1)
Mo(2)–Mo(1)–Cl(12)	120.3(2)	Mo(3)–Mo(1)–Cl(12)	124.5(1)
Se(1)–Mo(1)–Cl(12)	86.7(1)	Se(3)–Mo(1)–Cl(12)	91.8(1)
Cl(11)–Mo(1)–Cl(12)	82.3(2)	Mo(2)–Mo(1)–S(1)	54.9(1)
Mo(3)–Mo(1)–S(1)	93.6(1)	Se(1)–Mo(1)–S(1)	50.9(1)
Se(3)–Mo(1)–S(1)	132.2(1)	Cl(11)–Mo(1)–S(1)	84.1(2)
Cl(12)–Mo(1)–S(1)	134.6(2)	Mo(2)–Mo(1)–S(3)	95.2(1)
Mo(3)–Mo(1)–S(3)	54.6(1)	Se(1)–Mo(1)–S(3)	132.1(1)
Se(3)–Mo(1)–S(3)	51.0(1)	Cl(11)–Mo(1)–S(3)	83.5(2)
Cl(12)–Mo(1)–S(3)	139.1(2)	S(1)–Mo(1)–S(3)	81.4(1)
Mo(2)–Mo(1)–S(4)	54.3(1)	Mo(3)–Mo(1)–S(4)	53.7(1)
Se(1)–Mo(1)–S(4)	88.4(1)	Se(3)–Mo(1)–S(4)	85.4(1)
Cl(11)–Mo(1)–S(4)	163.3(1)	Cl(12)–Mo(1)–S(4)	81.1(2)
S(1)–Mo(1)–S(4)	109.1(2)	S(3)–Mo(1)–S(4)	108.0(2)
Mo(1)–Mo(2)–Mo(3)	60.3(1)	Mo(1)–Mo(2)–Se(1)	57.8(1)
Mo(3)–Mo(2)–Se(1)	118.1(1)	Mo(1)–Mo(2)–Se(2)	118.2(1)
Mo(3)–Mo(2)–Se(2)	58.1(1)	Se(1)–Mo(2)–Se(2)	173.3(1)
Mo(1)–Mo(2)–Cl(21)	120.4(1)	Mo(3)–Mo(2)–Cl(21)	124.1(1)
Se(1)–Mo(2)–Cl(21)	87.3(1)	Se(2)–Mo(2)–Cl(21)	90.8(1)
Mo(1)–Mo(2)–Cl(22)	138.3(1)	Mo(3)–Mo(2)–Cl(22)	138.2(1)
Se(1)–Mo(2)–Cl(22)	92.3(1)	Se(2)–Mo(2)–Cl(22)	93.8(1)
Cl(21)–Mo(2)–Cl(22)	82.2(2)	Mo(1)–Mo(2)–S(1)	54.9(1)
Mo(3)–Mo(2)–S(1)	93.6(1)	Se(1)–Mo(2)–S(1)	50.8(1)
Se(2)–Mo(2)–S(1)	132.8(1)	Cl(21)–Mo(2)–S(1)	135.0(2)
Cl(22)–Mo(2)–S(1)	84.0(2)	Mo(1)–Mo(2)–S(2)	96.0(1)
Mo(3)–Mo(2)–S(2)	54.8(1)	Se(1)–Mo(2)–S(2)	132.8(1)
Se(2)–Mo(2)–S(2)	50.9(1)	Cl(21)–Mo(2)–S(2)	137.9(2)
Cl(22)–Mo(2)–S(2)	83.7(2)	S(1)–Mo(2)–S(2)	82.1(2)
Mo(1)–Mo(2)–S(4)	53.9(1)	Mo(3)–Mo(2)–S(4)	53.7(1)
Se(1)–Mo(2)–S(4)	88.0(1)	Se(2)–Mo(2)–S(4)	85.4(1)
Cl(21)–Mo(2)–S(4)	81.3(2)	Cl(22)–Mo(2)–S(4)	163.5(2)
S(1)–Mo(2)–S(4)	108.6(2)	S(2)–Mo(2)–S(4)	108.1(2)
Mo(1)–Mo(3)–Mo(2)	59.5(1)	Mo(1)–Mo(3)–Se(2)	117.0(1)
Mo(2)–Mo(3)–Se(2)	57.6(1)	Mo(1)–Mo(3)–Se(3)	57.5(1)
Mo(2)–Mo(3)–Se(3)	116.9(1)	Se(2)–Mo(3)–Se(3)	170.1(1)
Mo(1)–Mo(3)–Cl(31)	124.2(1)	Mo(2)–Mo(3)–Cl(31)	124.6(2)
Se(2)–Mo(3)–Cl(31)	88.7(1)	Se(3)–Mo(3)–Cl(31)	88.6(1)
Mo(1)–Mo(3)–Cl(32)	137.7(1)	Mo(2)–Mo(3)–Cl(32)	138.0(1)
Se(2)–Mo(3)–Cl(32)	94.8(1)	Se(3)–Mo(3)–Cl(32)	94.2(1)
Cl(31)–Mo(3)–Cl(32)	80.7(2)	Mo(1)–Mo(3)–S(2)	95.3(1)
Mo(2)–Mo(3)–S(2)	54.6(1)	Se(2)–Mo(3)–S(2)	50.6(1)
Se(3)–Mo(3)–S(2)	134.9(1)	Cl(31)–Mo(3)–S(2)	134.7(2)
Cl(32)–Mo(3)–S(2)	83.6(1)	Mo(1)–Mo(3)–S(3)	54.7(1)
Mo(2)–Mo(3)–S(3)	94.7(1)	Se(2)–Mo(3)–S(3)	134.6(1)
Se(3)–Mo(3)–S(3)	50.9(1)	Cl(31)–Mo(3)–S(3)	134.9(2)
Cl(32)–Mo(3)–S(3)	83.3(2)	S(2)–Mo(3)–S(3)	84.3(1)
Mo(1)–Mo(3)–S(4)	53.6(1)	Mo(2)–Mo(3)–S(4)	54.0(1)
Se(2)–Mo(3)–S(4)	85.2(1)	Se(3)–Mo(3)–S(4)	85.0(1)
Cl(31)–Mo(3)–S(4)	83.5(2)	Cl(32)–Mo(3)–S(4)	164.2(1)
S(2)–Mo(3)–S(4)	108.2(2)	S(3)–Mo(3)–S(4)	107.9(2)
Mo(1)–Se(1)–Mo(2)	64.1(1)	Mo(1)–Se(1)–S(1)	59.8(1)
(Mo(2)–Se(1)–S(1)	59.7(1)	Mo(2)–Se(2)–Mo(3)	64.3(1)
Mo(2)–Se(2)–S(2)	59.7(1)	Mo(3)–Se(2)–S(2)	59.6(1)
Mo(1)–Se(3)–Mo(3)	64.5(1)	Mo(1)–Se(3)–S(3)	59.8(1)
Mo(3)–Se(3)–S(3)	59.5(1)	Mo(1)–S(1)–Mo(2)	70.2(1)
Mo(1)–S(1)–Se(1)	69.3(1)	Mo(2)–S(1)–Se(1)	69.5(1)
Mo(2)–S(2)–Mo(3)	70.6(1)	Mo(2)–S(2)–Se(2)	69.5(1)
Mo(3)–S(2)–Se(2)	69.8(1)	Mo(1)–S(3)–Mo(3)	70.7(1)
Mo(1)–S(3)–Se(3)	69.2(1)	Mo(3)–S(3)–Se(3)	69.6(1)
Mo(1)–S(4)–Mo(2)	71.9(1)	Mo(1)–S(4)–Mo(3)	72.7(1)
Mo(2)–S(4)–Mo(3)	72.4(1)		

and a thiocyanate (eqn. (2)).

$$Mo_3S_7X_6^{2-} + 3NCSe^- + 3NCS^- \longrightarrow Mo_3S_4Se_3(NCS)_6^{2-} + 6X^- \quad (2)$$

To isolate the individual reaction products in the case of halogenide complexes it is necessary to suppress formation of the halogen–thiocyanate mixed-ligand complexes. This is best achieved by adding a large excess of KSCN. A special experiment indicated that the presence in the solution at the same time of both $SeCN^-$ and SCN^- (in a mole ratio of at least 1:85) did not suppress substitution at the disulfide ligand. On the other hand, attempts to use a large excess of selenocyanate without addition of thiocyanate ($Mo_3/SeCN^- = 1:15$) failed to afford analytically pure complexes $Mo_3S_4Se_3(NCSe)_6^{2-}$, presumably because of competition between the selenocyanate and the forming thiocyanate for coordination to the metal.

To prove the structure of $Mo_3S_4Se_3(NCS)_6^{2-}$ the following preparative evidence was used.

1. A parallel synthesis from $(Et_4N)_2Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_aSe_e)_3Cl_6$ [10] produced the same product **I**.
2. The reaction of $(Et_4N)_2Mo_3S_7(NCS)_6$ with Ph_3PSe also results in **I**.
3. Treatment of **I** with concentrated HCl also produces $(Et_4N)_2Mo_3S_4Se_3Cl_6$.

Since it was not possible to obtain **I** as single crystals it was transferred to the chloride complex $(PPN)_2Mo_3S_4Se_3Cl_6$ (**IIIb**). The structure of the latter has been determined by X-ray structural analysis so that the equatorial position of the selenium atom of the μ_2-SSe ligand was completely established.

The structure of the $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}SSe)_3Cl_6^{2-}$ anion of this salt is practically the same as that described earlier for $(Ph_3PEt)_2Mo_3S_4Se_3Cl_6$ [10] as is readily seen from the values of the interatomic distances and the bond angles (Tables 1 and 2). The structure of the anion is shown in Fig. 1.

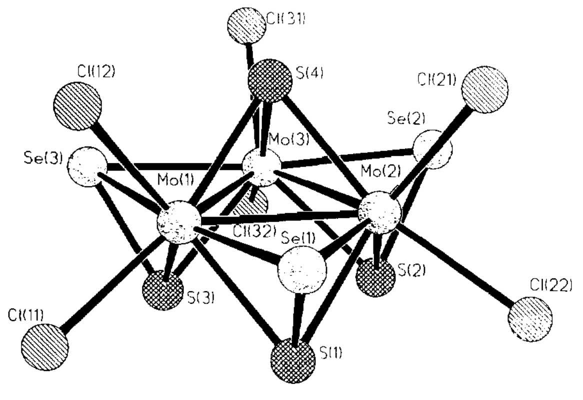


Fig. 1. Structure of the $Mo_3S_4Se_3Cl_6^{2-}$ anion.

The Mo atoms form an almost equilateral triangle with Mo–Mo distances of 2.765(2)–2.787(2) Å and S–Se distances of 2.156(5)–2.166(3) Å. The equatorial atoms of the μ_2-SSe selenium practically lie in the same plane as Mo_3, deviating from it by not more than 0.2 Å (Table 3). The coordinates of the non-hydrogen atoms are given in Table 4.

The isotope exchange with KSCN

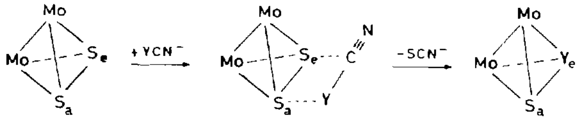
Earlier [10] we discovered differences in reactivity between Ph_3PSe and Ph_3PS: unlike the former, the latter does not undergo sulfur substitution in the μ_2-S_2 ligands of $Mo_3S_7X_6^{2-}$. In the case of $NCSe^-$ and NCS^- the situation is different: the thiocyanate turns out to be capable of undergoing isotope exchange (eqns. (3) and (4))

$$(Et_4N)_2Mo_3S_7Cl_6 + 6KSCN = (Et_4N)_2Mo_3S_7(NCS)_6 + 6KCl \quad (3)$$

$$(Et_4N)_2Mo_3{}^{34}S_7Cl_6 + 6KSCN = (Et_4N)_2Mo_3{}^{34}S_4S_3(NCS)_6 + 6KCl \quad (4)$$

However, the S → Se exchange is thermodynamically still more favored and an almost hundred-fold excess of thiocyanate with respect to the selenocyanate does not suppress reaction (2).

The following scheme may be proposed for the reactions with KYCN (Y = S, Se):



Of course, this scheme is only tentative and the reactions must not necessarily proceed simultaneously. In this case YCN^- must behave as a nucleophile since earlier the μ_2-S_2 group has been shown by us to be highly stable towards electrophilic attack (can stand the action of H^+, halogens [11]). A possible alternative mechanism of elimination–addition cannot be totally excluded [9]. While $(Et_4N)_2Mo_3{}^{34}S_7Cl_6$ with KSCN gives the same product of isotopic ex-

TABLE 3. Deviation of the $Mo_3S_4Se_3Cl_6^{2-}$ dianion atoms from the plane of the three Mo atoms

Atom	Deviation (Å)	Atom	Deviation (Å)
Se1	0.048	Cl31	1.864
Se2	0.201	Cl32	−1.311
Se3	0.176	S1	−1.715
Cl11	−1.265	S2	−1.643
Cl12	1.921	S3	−1.659
Cl21	1.911	S4	1.724
Cl22	−1.258		

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq}[a]
Mo(1)	−4161(1)	2510(1)	−23(1)	28(1)
Mo(2)	−6029(1)	1982(1)	338(1)	29(1)
Mo(3)	−4176(1)	1627(1)	1045(1)	30(1)
Se(1)	−5914(1)	2837(1)	−632(1)	43(1)
Se(2)	−5919(2)	1266(1)	1427(1)	45(1)
Se(3)	−2398(1)	2248(1)	735(1)	41(1)
Cl(11)	−3749(4)	2474(3)	−1207(3)	51(2)
Cl(12)	−2988(3)	3980(2)	328(3)	50(2)
Cl(21)	−6517(4)	2971(3)	1015(3)	53(2)
Cl(22)	−8141(3)	1245(3)	−365(3)	47(2)
Cl(31)	−2902(4)	2196(3)	2445(3)	59(2)
Cl(32)	−3812(3)	390(3)	1261(3)	47(2)
S(1)	−6067(3)	1595(2)	−947(2)	36(2)
S(2)	−6115(3)	629(2)	290(2)	36(2)
S(3)	−3938(3)	1239(2)	−142(2)	34(2)
S(4)	−4169(3)	2942(2)	1209(2)	35(2)
P(1)	1923(3)	3710(2)	3093(2)	33(2)
P(2)	2843(3)	4909(2)	2341(2)	34(2)
P(3)	−78(3)	−1915(2)	3417(2)	35(2)
P(4)	1198(3)	−383(2)	3192(2)	34(2)
N(1)	2839(10)	4337(7)	2891(7)	35(6)
N(2)	992(10)	−1093(7)	3585(7)	37(6)
C(1)	2705(15)	3586(9)	3997(9)	42(8)
C(2)	3893(15)	3966(11)	4348(10)	57(9)
C(3)	4485(18)	3832(14)	5039(12)	84(12)
C(4)	3894(21)	3317(13)	5368(12)	79(13)
C(5)	2692(20)	2934(13)	5016(12)	71(12)
C(6)	2122(16)	3052(11)	4331(10)	55(10)
C(7)	1157(12)	2713(8)	2390(8)	30(7)
C(8)	1656(15)	2426(10)	1939(10)	46(9)
C(9)	1077(21)	1689(12)	1376(11)	67(13)
C(10)	−18(17)	1180(10)	1238(10)	53(10)
C(11)	−510(15)	1437(11)	1695(11)	52(9)
C(12)	68(14)	2196(9)	2261(10)	42(9)
C(13)	852(14)	4045(9)	3202(10)	40(8)
C(14)	−70(14)	3941(10)	2532(11)	46(9)
C(15)	−814(18)	4267(13)	2603(14)	69(13)
C(16)	−657(21)	4700(14)	3318(17)	75(15)
C(17)	247(23)	4815(12)	3976(14)	77(15)
C(18)	1029(16)	4480(10)	3939(10)	49(9)
C(19)	4044(13)	5078(9)	2086(9)	37(8)
C(20)	3969(15)	5168(10)	1371(10)	49(9)
C(21)	4901(21)	5295(13)	1182(14)	77(14)
C(22)	5859(21)	5289(14)	1687(18)	89(17)
C(23)	5959(17)	5207(15)	2399(16)	84(14)
C(24)	5042(15)	5106(11)	2622(12)	58(10)
C(25)	2966(13)	5900(9)	2822(8)	35(7)
C(26)	3251(17)	6549(11)	2517(11)	56(11)
C(27)	3218(21)	7273(12)	2824(12)	72(13)
C(28)	2910(18)	7355(11)	3435(12)	67(11)
C(29)	2607(16)	6731(11)	3734(10)	55(10)
C(30)	2677(16)	6010(9)	3452(10)	54(9)
C(31)	1578(12)	4490(9)	1444(9)	33(7)
C(32)	1313(14)	3731(10)	949(10)	44(9)
C(33)	299(16)	3328(11)	306(11)	54(10)
C(34)	−468(14)	3700(12)	138(9)	54(9)
C(35)	−200(15)	4454(12)	595(12)	57(11)
C(36)	807(14)	4855(10)	1261(10)	44(8)
C(37)	−576(13)	−2673(9)	2500(9)	37(8)
C(38)	−467(14)	−3422(10)	2458(9)	42(8)
C(39)	−867(17)	−3992(10)	1741(11)	57(10)
C(40)	−1370(15)	−3834(10)	1046(10)	49(9)
C(41)	−1459(13)	−3083(10)	1094(9)	41(8)
C(42)	−1075(14)	−2521(9)	1809(9)	39(8)
C(43)	345(14)	−2334(10)	4203(9)	41(9)
C(44)	1439(15)	−1978(10)	4773(10)	47(9)
C(45)	1765(17)	−2280(13)	5395(10)	59(11)
C(46)	944(20)	−2972(13)	5425(11)	65(12)
C(47)	−133(18)	−3340(11)	4850(11)	59(11)
C(48)	−452(16)	−3027(11)	4242(10)	52(10)
C(49)	−1332(14)	−1771(9)	3445(9)	37(10)
C(50)	−1160(15)	−1101(10)	4021(10)	49(9)
C(51)	−2064(19)	−968(12)	4079(12)	62(12)
C(52)	−3129(22)	−1509(16)	3566(15)	80(15)
C(53)	−3318(16)	−2177(15)	2993(13)	76(13)
C(54)	−2408(15)	−2316(11)	2919(10)	52(9)
C(55)	1201(12)	−690(9)	2265(9)	36(7)
C(56)	1591(14)	−1289(10)	2101(10)	47(8)
C(57)	1775(16)	−1469(12)	1431(11)	56(10)
C(58)	1553(16)	−1041(13)	900(12)	66(11)
C(59)	1178(16)	−447(12)	1038(10)	55(10)
C(60)	1013(15)	−277(10)	1712(9)	46(9)
C(61)	249(12)	121(9)	3147(9)	33(7)
C(62)	526(15)	749(9)	3815(9)	43(9)
C(63)	−270(17)	1062(11)	3844(10)	52(10)
C(64)	−1338(16)	742(10)	3236(11)	51(10)
C(65)	−1602(14)	111(11)	2587(11)	53(10)
C(66)	−826(13)	−214(10)	2533(9)	38(8)
C(67)	2601(13)	392(10)	3790(10)	44(8)
C(68)	2975(20)	1085(14)	3565(14)	92(14)
C(69)	4052(25)	1688(18)	3973(19)	131(18)
C(70)	4763(22)	1600(20)	4606(18)	122(17)
C(71)	4408(22)	916(20)	4861(16)	117(17)
C(72)	3331(15)	335(12)	4447(12)	66(10)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

change $(Et_4N)_2Mo_3(\mu_3\text{-}^{34}S)(\mu_2\text{-}^{34}S_aS_e)_3(NCS)_6$ both at room and boiling temperature, a rather different situation occurs in the case of tungsten. $(Et_4N)_2W_3S_7(NCS)_6$ can be produced only at room temperature. Under heating sulfur elimination took place and $(Et_4N)_5W_3S_4(NCS)_9$ was obtained in high yield (eqns. (5) and (6))

$$(Et_4N)_2W_3S_7Br_6 + 6KSCN \longrightarrow \underset{\textbf{(IV)}}{(Et_4N)_2W_3S_7(NCS)_6} + 6KBr \quad (5)$$

$$(Et_4N)_2W_3S_7Br_6 + 9KSCN + 3Et_4NBr \longrightarrow \underset{\textbf{(V)}}{(Et_4N)_5W_3S_4(NCS)_9} + 3S + 9KBr \quad (6)$$

Complex **IV** can be converted into **V** when boiling in CH_3CN only in the presence of KSCN.

Vibrational spectra

In Fig. 2 the vibrational spectra of $(Et_4N)_2Mo_3S_4Se_3(NCS)_6$ (**I**) and $(Et_4N)_2Mo_3S_7(NCS)_6$ (**IIa**) are shown. The isotope shifts observed on going from **IIa** to **IIb** are listed in Table 5. The cluster cores $Mo_3S(S_2)_3^{4+}$ and $Mo_3S(SSe)_3^{4+}$ are coordinated to six thiocyanate ligands via nitrogen atoms. This is supported by the presence in the IR spectra of bands at 2080 and 470 cm^{-1} characteristic of such a type of coordination [16]. In the Raman spectra the μ_2-SSe and μ_2-S_2 ligands appear as intense characteristic bands [9–11] at 482 cm^{-1} in **I** and at 549 cm^{-1} in **IIa**. In the reaction of $(Et_4N)_2Mo_3{}^{34}S_7Cl_6$ with KSCN $(Et_4N)_2Mo_3(\mu_3\text{-}{}^{34}S)(\mu_2\text{-}{}^{34}S^{32}S)_3(NCS)_6$ (**IIb**) was produced. This conclusion was based on the observation that upon going from **IIa** to **IIb** there is shift of ν(S–S) by 8 cm^{-1} [9, 11].

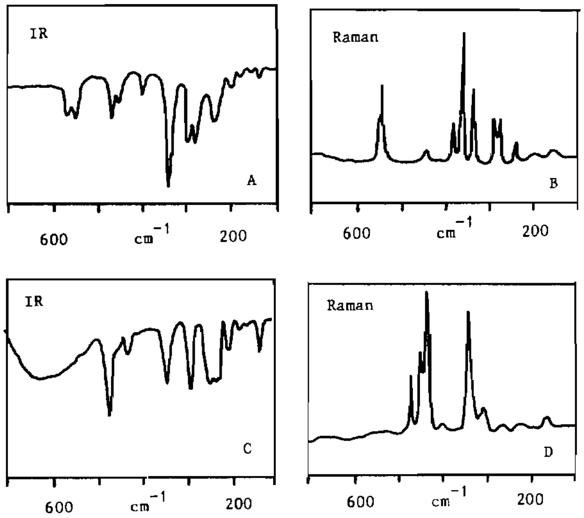


Fig. 2. IR and Raman spectra of $(Et_4N)_2Mo_3S_7(NCS)_6$ (A and B) and $(Et_4N)_2Mo_3S_4Se_3(NCS)_6$ (C and D).

TABLE 5. Experimental vibrational frequencies in the IR and Raman spectra of the $(Et_4N)_2Mo_3S_7(NCS)_6$ complex and their shifts upon isotope exchange

IIa (cm^{-1})	**IIa**$\rightarrow$**IIb** (cm^{-1})
558 IR	8
549 IR, Raman	8
469 IR	3
452 IR, Raman	6
397 IR	4
386 Raman	4
360 Raman	2
340 IR, Raman	4
298 IR, Raman	1
287 IR	1
283 Raman	2
236 IR	2

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