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RETENTION OF THIO- AND SELENOMETALATES IN MOBILE-PHASE ION CHROMATOGRAPHY

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SUMMARY

Mobile-phase ion chromatography (MPIC) with suppressed conductivity and UV detection provides an efficient technique for the analysis of thio- and selenometalates in mixtures. A porous resin, derived from divinylbenzene, was used as the stationary phase. Tetrabutylammonium hydroxide was used as the ion-pair reagent.

The retention model proposed by Bidlingmeyer *et al.* was applied to explain the parabolic increase of ln k' with increasing degree of replacement of oxygen by sulphur or selenium, respectively, in the metal oxyanions.

Other compounds investigated include poly(thiometalates) formed by intramolecular redox condensation of oxothiometalates and also various bi- and trinuclear molybdenum sulphur clusters, for which MPIC conditions were established. Retention parameters, such as hydrophobicity and solvophobic surface area, are discussed to explain the different retention behaviours of these compounds.

INTRODUCTION

Transition metals of low electron density, such as tungsten and molybdenum, form tetrahedral thio- and selenoanions of various colours with remarkable properties as bidentate ligands[1]. Thiometalates permit the formation of multi-metal complexes that have interesting structures and/or unique electronic properties. In certain complexes, four-membered metal–sulphur ring systems, MS_2M', with different formal valencies of M and M′ and metal–metal interactions have been identified. Further, poly(thiometalates) with mixed valencies are derived from thiometalates via novel redox processes and simultaneous condensation.

The relevance of thiomolybdates and -tungstates, particularly of the MoS_4^{2-} ion, in modelling biological systems has recently been recognized[2]. Tetrathiomolybdate is formed, for instance, as one product of the acid–base hydrolysis of the Mo-Fe-protein (MoF-p) of *Clostridium pasteurianum*[3] and therefore it plays an important

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role in our understanding of the nitrogenase problem. In fact, studies on both nitrogenase and its iron–molybdenum cofactor have shown that both MoS_4^{2-} and $MoOS_3^{2-}$ can be liberated under proper degradative conditions.

Thiomolybdates are probably formed in the digestive tract of ruminants[4] and also seem to be associated with some disorder of copper metabolism in men. In general, the MoS_4^{2-} ion is recognized as the strongest antagonist for copper metabolism. The high molybdenum content in soil can be responsible for copper deficiency disease in ruminants, presenting a serious problem for animal nutrition.

In the past, thiometalates have been characterized using a combination of infrared and UV–VIS spectroscopy. Diemann and Müller[5] provided a compilation of these data, together with resonance Raman and structural data. They also discussed in detail the bonding and spectroscopy of these species in terms of molecular orbital theory. The utility of the UV–VIS spectra of thio- and selenometalates in determining purity is only valuable for ions such as WS_4^{2-}, where contamination by WOS_3^{2-} is common. Because the major peak in the electronic spectrum of WOS_3^{2-} (334 nm) occurs at a minimum in the spectrum of WS_4^{2-}, this impurity is readily detected. For other compounds, such as $MoOS_3^{2-}$, contamination with MoS_4^{2-} can only be recognized by measuring the intensity ratios of the peaks at 395 and 457 nm[6], whereas the determination of various thio- and selenometalates in mixtures is not possible by spectroscopic means. On the other hand, precise analytical data for these compounds are becoming increasingly important as these ions play a vital role in bioinorganic research. Their quantitation as degradation products of molybdenum-containing enzymes by means of liquid chromatography has not been reported so far. It is the purpose of this paper to describe an ion chromatographic method for the determination of thio- and selenometalates and also for disulphido complexes of molybdenum(IV) and -(V) utilizing mobile-phase ion chromatography (MPIC)[7], and to report the investigation of their retention characteristics.

EXPERIMENTAL

All experiments were performed on a Dionex 4020i liquid chromatograph (Dionex, Sunnyvale, CA, U.S.A.), equipped with a quaternary gradient pump, a UV–VIS absorbance detector and a conductivity detector. Unless specified otherwise, the analytes were dissolved in aqueous sodium hydroxide solution (pH 11). The sample loop size was 50 μl. The eluent and detection modes were chosen according to the nature of the sample. Data were collected with an SP 4270 computing integrator set at 1 V input (Spectra-Physics, Darmstadt, F.R.G.). The separation columns used included a 25 cm × 4 mm I.D. HPIC-AS5 and a 20 cm × 4 mm I.D. MPIC-NS1 column (both from Dionex). The column dead time was determined with sodium hydroxide solution (pH 11).

Water for the eluent was purified in a Barnstead PCR still (Barnstead, Boston, MA, U.S.A.). The ion-pair reagent was purchased from Dionex, the modifier acetonitrile from Promochem (Wesel, F.R.G.), sodium carbonate, sodium hydrogencarbonate and sodium tungstate from Merck (Darmstadt, F.R.G.) and sodium molybdate from Aldrich (Milwaukee, WI, U.S.A.).

Thio- and selenometalates were prepared according to methods described by McDonald *et al.*[6] and Müller and Diemann[8], respectively.

$[(CH_3)_4N]_2[Mo_2O_2S_2(S_2)_2]$ was prepared following the procedure of Müller and coworkers[9,10]. The preparation of disulphido complexes, such as $[(NH_4)_2][Mo_2S_{12}]$ and $[(NH_4)_2][Mo_3S_{13}]$, has also been described by Müller *et al.*[11].

Preparation of $[(PPh_4)_2][MoS_9]$[12]

A dimethylformamide (analytical-reagent grade) solution (30 ml) containing 2 g of $(PPh_4)_2MoS_4$ (2.2 m*M*) and 0.5 g of sulphur (15.6 m*M*) was stirred for 10 min under nitrogen at 20°C. After filtration, 5 ml of diethyl ether were added to the reaction mixture, which was then stored in a closed flask under nitrogen at 5–7°C. The crystals of $[(PPh_4)_2][MoS_9]$ were filtered after 2–3 days and washed with 2-propanol and diethyl ether and dried in a stream of nitrogen. The yield was about 0.25 g (10%).

Preparation of $[(PPh_4)_2][Mo_2S_{10}]$[12]

A stirred dimethylformamide (analytical-reagent grade) solution containing 0.9 g of $(PPh_4)_2MoS_4$ (1 m*M*), after addition of 128 mg of sulphur (4 m*M*), was heated under nitrogen for 10 min at 153°C. The reaction mixture was allowed to cool to 20°C, filtered, 10 ml of diethyl ether were added and the mixture was then stored in a closed flask under nitrogen at 5–7°C. The crystals of $[(PPh_4)_2][Mo_2S_{10}]$ were filtered after 3 days and washed with 2-propanol and diethyl ether and dried in a stream of nitrogen. The yield was about 0.5 g (42%).

RESULTS AND DISCUSSION

Thiomolybdates and thiotungstates

The syntheses of thiomolybdates and thiotungstates involve the exhaustive treatment of molybdate and tungstate solutions with hydrogen sulphide in concentrated ammonia solution[6]. Molybdate and tungstate and also other metal oxyanions can be separated by anion-exchange chromatography[7]. Owing to their large radii, these ions have a high affinity for the stationary phase. Using a special latexed anion exchanger, HPIC-AS5, with a surface-sulphonated polystyrene–divinylbenzene core and hydrophilic functional groups on the latex particles, the separation of polarizable anions can be carried out with carbonate–hydrogencarbonate eluents. In order to minimize adsorption effects, a small amount of *p*-cyanophenol can be added to the eluent. The eluent system is compatible with membrane-based suppressor systems, hence the most sensitive detection system for metal oxyanions is suppressed conductivity detection[7]. An example of the chromatographic separation of molybdate and tungstate is shown in Fig. 1.

Passing hydrogen sulphide into aqueous solutions of molybdate and tungstate successively replaces oxygen by sulphur, forming thiomolybdates and thiotungstates, respectively. With an increasing degree of replacement of oxygen by sulphur, the affinity of these sulphur-containing anions to the stationary phase increases dramatically. The retention gain per sulphur atom is so strong that even MoO_3S^{2-} cannot be eluted with carbonate–hydrogencarbonate eluents from an anion exchanger within a reasonable time. For the separation of thiometalates we therefore developed an ion-pair chromatographic method utilizing a non-derivatized divinylbenzene-based porous resin which has a high specific surface area of *ca.* 350 m^2/g. Owing to its

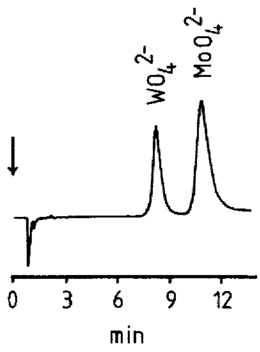


Fig. 1. Separation of tungstate and molybdate utilizing anion-exchange chromatography. Separator, HPIC-AS5; eluent, 0.0028 *M* $NaHCO_3$ + 0.0022 *M* Na_2CO_3; suppressed conductivity detection; flow-rate, 2 ml/min; solute concentration, 50 mg/l WO_4^{2-} and MoO_4^{2-}.

structural elements (alkyl residues and benzene rings), it is only slightly polar and essentially hydrophobic. For separating surface-inactive anions, such as thiometalates, tetrabutylammonium hydroxide proved to be the most suitable ion-pair reagent. To support ion-pair formation in the mobile phase and to adjust the eluent polarity, acetonitrile is added to the eluent in small amounts. As shown in Fig. 2, all anions, $MoO_nS_{4-n}^{2-}$ (n = 0–4), under investigation can be separated isocratically with this technique. Although all thiomolybdates can be characterized by direct UV detection at 254 nm[5], suppressed conductivity detection was employed in this instance to com-

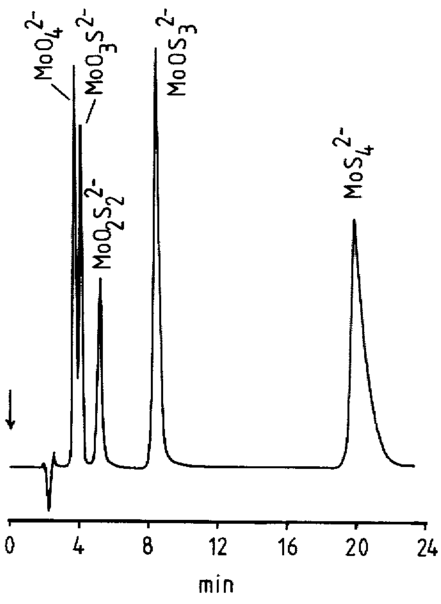


Fig. 2. Separation of molybdate and its thia-substituted derivatives. Separator, MPIC-NS 1; eluent, 0.001 *M* Na_2CO_3 + 0.002 *M* tetrabutylammonium hydroxide–acetonitrile (75:25, v/v); suppressed conductivity detection; flow-rate, 1 ml/min; solute concentration, 50 mg/l $(NH_4)_2MoO_4$, 200 mg/l $(NH_4)_2MoO_2S_2$, $(NH_4)_2MoOS_3$ and $(NH_4)_2MoS_4$.

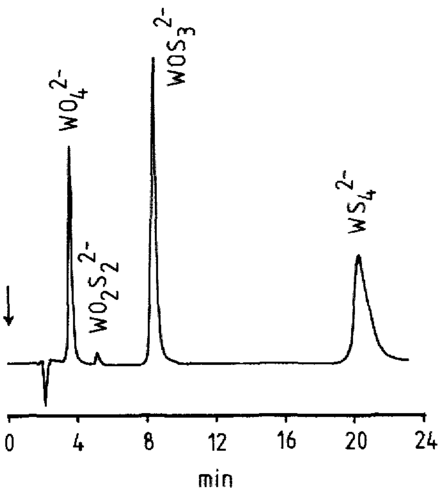


Fig. 3. Separation of tungstate and its thia-substituted derivatives. Chromatographic conditions as in Fig. 1; solute concentration, 100 mg/l $Na_2WO_4 \cdot 2H_2O$ and Cs_2WOS_3, 200 mg/l $(NH_4)_2WS_4$.

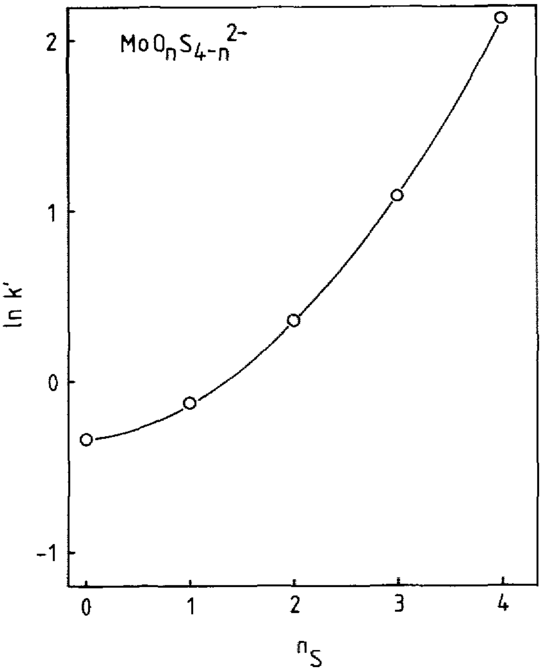


Fig. 4. Increase in ln k' as a function of increasing number of sulphur atoms, n_S, in thiomolybdates, $MoO_nS_{4-n}^{2-}$.

pare the retention times of the non-absorbing molybdate and the respective thioanions.

Thiotungstates, $WO_nS_{4-n}^{2-}$ (n = 0–4), were separated under the same chromatographic conditions (Fig. 3). The retention times of the various thiotungstates are almost identical with those of the respective thiomolybdates, because the ionic radii of both Mo^{6+} and W^{6+} are identical. Therefore, molybdenum- and tungsten-containing anions of the same structure cannot be separated by MPIC. On the other hand, the separation and detection system described here is suitable for determining thiometalates in complex mixtures (reaction control) and for investigating the purity of single components (product control).

From Figs. 2 and 3, it is clear that the retention of thiometalates increases with increasing degree of replacement of oxygen by sulphur. For the series of thiomolybdates, a plot of ln k' *versus* the number of sulphur atoms, n_S, is shown in Fig. 4, indicating a parabolic increase of ln k' with n_S. The respective data are listed in Table I.

According to the retention model proposed by Bidlingmeyer *et al.*[13], we assume that the surface of the MPIC stationary phase is occupied by acetonitrile molecules and tetrabutylammonium ions, the surface density of which depends on their concentration in the bulk mobile phase. Thus, the layer adsorbed at the stationary phase has a positive excess charge. This is compensated for by an adjacent diffuse region which contains water, acetonitrile, OH^- and anions to be analysed. Compared with the bulk solution, this region contains an excess negative charge, thus completing the electric double layer.

The concentration of acetonitrile is highest in the direct vicinity of the stationary surface and decreases to the bulk mobile phase concentration across the double layer. The water concentration gradient has the opposite direction. The retention of ions in MPIC depends not only on their charge but also on their more or less pronounced solvophobic properties. Once an ion pair has formed at the surface of the stationary phase, its affinity for that phase is largely governed by non-ionic interactions. The same holds for the reluctance of sorbed ions to re-enter the more aqueous bulk mobile phase.

The electric charge of all anions, $MoO_nS_{4-n}^{2-}$, under investigation is the same. The main parameters governing non-ionic interactions are solute molecular surface area and the ability of the solute to undergo intermolecular interactions with the eluent and the stationary phase.

TABLE I

ln k' VALUES FOR MOLYBDATE AND ITS THIA-SUBSTITUTED DERIVATIVES

For chromatographic conditions, see Fig. 2.

Species	*ln k'*
MoO_4^{2-}	−0.34
MoO_3S^{2-}	−0.13
$MoO_2S_2^{2-}$	0.35
$MoOS_3^{2-}$	1.08
MoS_4^{2-}	2.12

The total surface area, TSA, and the respective contributions SA(Mo, W), SA(O) and SA(S) of the constituents were calculated according to Pearlman's method[14,15]. From structural analysis data[5] it appears that all relevant ions have a symmetry close to tetrahedral. The Mo–S bond length is 2.17 Å on average and the Mo–O bond length 1.785 Å. The Van der Waals radii were replaced by the ionic radii (0.62 Å for both Mo^{6+} and W^{6+}, 1.32 Å for O^{2-} and 1.84 Å for S^{2-}). The result is shown in Fig. 5. It is seen that the metal surface area contribution is almost negligible. The total surface area increases with increasing degree of replacement of oxygen by sulphur, not quite linearly, but it can reasonably well approximated by

$$TSA = 90.743 + 17.481\, n_S \qquad (r = 0.9986) \tag{1}$$

The small deviation from linearity is negative, which would slightly diminish rather than increase the retention gain per sulphur atom. It certainly does not account for the parabolic increase in ln k' with n_S.

From other investigations[16], it is known that the electron lone pairs of oxygen maintain a strong hydrogen bond interaction with polar solvents such as water. The lone pairs of sulphur atoms in the tetrahedral state do not have this property. Sulphur atoms, chains and rings are extremely solvophobic even in pure methanol. This is not necessarily true if the electron density or distribution around the sulphur atom is appreciably changed.

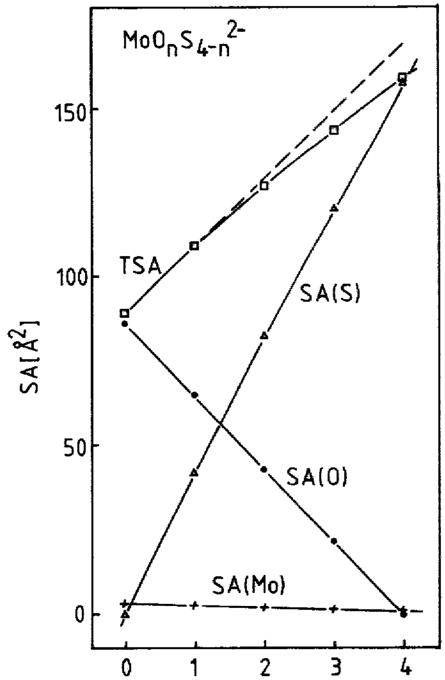


Fig. 5. Surface area contributions (SA) of molybdenum, oxygen and sulphur in thiomolybdates, $MoO_4S^{2-}_{4-n}$.

From the high retention of MoS_4^{2-} in MPIC we have to conclude that in this ion the sulphur atoms are strongly solvophobic. Because of the tetrahedral symmetry, all sulphur atoms are equivalent and contribute identically to retention:

$$\ln k'(MoS_4^{2-}) = 4\Delta_S \tag{2}$$

where Δ_S is the ln k' contribution of one sulphur atom.

If one sulphur atom is replaced by oxygen, it is not only the reduction of TSA and the exchange of the solvophobic surface by a more solvophilic surface that lowers the retention. The introduction of strongly electronegative oxygen changes the electronic states of the remaining sulphur atoms so that they become more solvophilic:

$$\ln k'(MoOS_3^{2-}) = 3(\Delta_S - D) + \Delta_O \tag{3}$$

where Δ_O is the ln k' contribution of one oxygen atom and D is the solvophobicity loss of sulphur atoms per oxygen atom present.

If all sulphur atoms are replaced by oxygen, we have

$$\ln k'(MoO_4^{2-}) = 4\Delta_O \tag{4}$$

Eqn. 3 can be generalized to yield

$$\ln k' = (\Delta_S + Dn_S - 4D)n_S + \Delta_O(4 - n_S) \tag{5}$$

which contains a quadratic term in n_S. From the experimental data given in Table I we obtain $\Delta_S = 0.53$, $\Delta_O = -0.0825$ and $D = 0.1388 \pm 0.003$. When inserted into eqn. 5, these values reproduce the experimental values perfectly (see Table II).

It should be pointed out that Δ_S and Δ_O are relative figures, as the contribution of the (unknown) phase ratio Φ has been omitted.

Selenotungstates

By analogy with the preparation of thiotungstates, selenotungstates are obtained by passing hydrogen selenide gas into an aqueous solution of tungstate, replacing oxygen successively by selenium. Fig. 6 shows a chromatogram of the sele-

TABLE II

EXPERIMENTAL AND THEORETICAL ln k' VALUES FOR MOLYBDATE AND ITS THIA-SUBSTITUTED DERIVATIVES

For chromatographic conditions, see Fig. 2.

Species	n_S	*ln k' (exp.)*	*ln k' (calc.)*
MoO_4^{2-}	0	−0.33	−0.33
MoO_3S^{2-}	1	−0.13	−0.13
$MoO_2S_2^{2-}$	2	0.35	0.34
$MoOS_3^{2-}$	3	1.08	1.09
MoS_4^{2-}	4	2.12	2.12

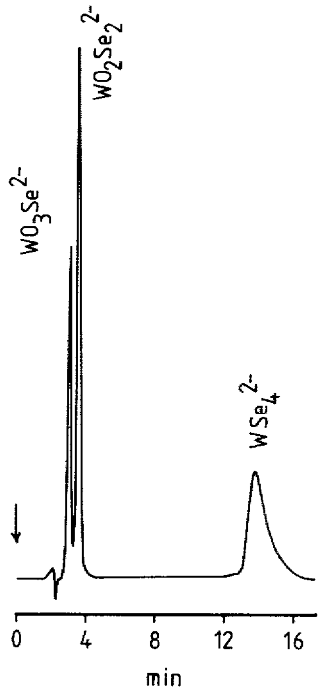


Fig. 6. Separation of tungstate and its selena-substituted derivatives. Separator, MPIC-NS 1; eluent, 0.001 *M* Na_2CO_3 + 0.002 *M* tetrabutylammonium hydroxide–acetonitrile (62:38, v/v); UV detection at 254 nm; flow-rate, 1 ml/min; solute concentration, 100 mg/l $(NH_4)_2WO_2Se_2$ and 150 mg/l $(NH_4)_2WSe_4$.

notungstates, $WO_nSe_{4-n}^{2-}$, under investigation, which can also be eluted isocratically from the MPIC separator. The amount of acetonitrile added to the mobile phase has to be increased significantly, because the retention of selenotungstates is much higher than that of the corresponding thiotungstates. The lower retention of thiotungstates compared with that of selenotungstates with an equal number of chalcogen atoms is related to the difference in the molecular surface area contributions of the respective chalcogen atoms. Thus, a selenium atom is much more effective in producing retention than a sulphur atom in the respective thiotungstate. A similar effect was observed by Möckel *et al.*[17] when investigating the retention of dialkyl polysulphides, RS_nR', and dialkyl polyselenides, RSe_nR', in reversed-phase liquid chromatography. Möckel *et al.* showed that for a given number of atoms, n_X, in the chalcogene chain, the retention of the polyselenide is higher than that of the polysulphide, indicating a difference in the surface area contributions of the respective chain elements.

Owing to their strong UV absorbance[5], the selenotungstates shown in Fig. 6 have been characterized by direct UV detection at 254 nm. In Fig. 7 the absolute retention, ln k', for the series of selenotungstates is displayed as a function of the number of selenium atoms, also indicating a parabolic increase in ln k' with n_{Se}. However, as data are available only for $WOSe_3^{2-}$, $WO_2Se_2^{2-}$ and WSe_4^{2-}, the plot in Fig. 7 is less reliable. The data are listed in Table III. The explanation for the parabolic increase in ln k' with n_{Se} follows that given for the thiotungstates and thiomolybdates mentioned above.

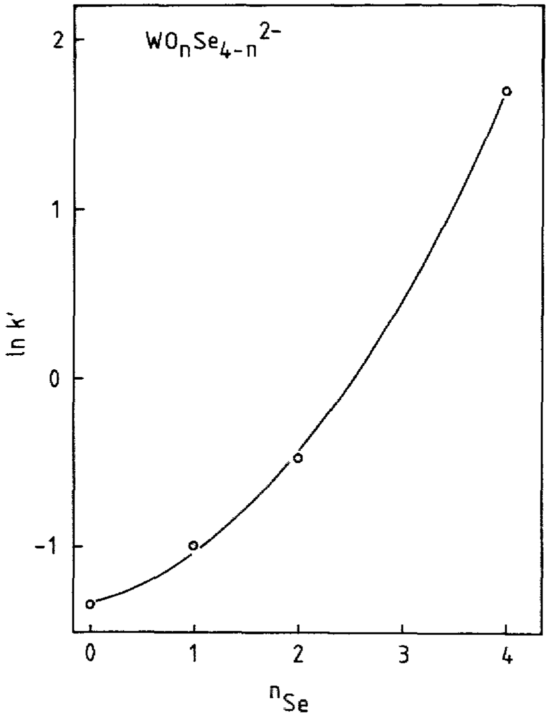


Fig. 7. Increase in ln k' as a function of increasing number of selenium atoms, n_{Se}, in selenotungstates, $WO_nSe_{4-n}^{2-}$.

TABLE III

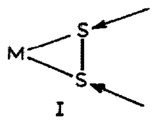
ln k' VALUES OF TUNGSTATE AND ITS SELENA-SUBSTITUTED DERIVATIVES

For chromatographic conditions, see Fig. 6.

Species	*ln k'*
WO_4^{2-}	−1.34
WO_3Se^{2-}	−0.98
$WO_2Se_2^{2-}$	−0.48
WSe_4^{2-}	1.69

Poly(thiometalates)

Aqueous solutions containing thiometalates are only stable in alkaline media; at neutral pH they are subject to hydrolysis[18]. Mixed oxothiometalates, such as $MoO_2S_2^{2-}$, exhibit a marked polymerization tendency in aqueous solutions, because the proton affinity of O is significantly higher than that of S. $Mo^{VI}O_2S_2^{2-}$ ions condensate under physiological conditions to the binuclear complex $[Mo^{V}_2O_2S_2(S_2)_2]^{2-}$ with η-S_2^{2-} ligands[9,10]. This complex of the side-on coordination type I:



I

is formed by intramolecular redox processes. The following reactions are assumed to be involved:

$$2\,S^{2-} \xrightarrow{Ox} S_2^{2-} \tag{6}$$

$$\begin{aligned} Mo^{VI} &\xrightarrow{Red} Mo^{IV} \\ (Mo^{VI} + Mo^{IV} &\xrightarrow{\quad} 2\,Mo^{V}) \end{aligned} \tag{7}$$

Hence formally an S_2^{2-} ligand is generated by oxidation of two S^{2-} ligands with reduction of molybdenum. The formation of an Mo–η-S_2 grouping has been ascertained by a complete X-ray structural analysis of the tetramethylammonium salt and by IR, Raman-, UV–VIS and ESCA spectroscopy[19]. Chromatographic data have not previously been published. For a better understanding of the kinetics involved in the redox condensation of $MoO_2S_2^{2-}$, the poly(thiometalate) $[Mo_2O_2S_2(S_2)_2]^{2-}$ was separated by means of mobile-phase ion chromatography utilizing direct UV detection at 254 nm. Fig. 8 shows a chromatogram of the respective tetramethylammonium salt. To elute this compound under isocratic conditions within a reasonable analysis time, the amount of acetonitrile added to the mobile phase had to be increased. Under these chromatographic conditions the mononuclear compound $MoO_2S_2^{2-}$ elutes in the void volume. To increase the resolution for the early eluting oxothiomolybdate while also eluting the more strongly retained poly(thiomolybdate), gradient elution was applied. Gradient elution is accomplished by maintaining the concentration of the ion-pair reagent constant and increasing the amount of acetonitrile during the run.

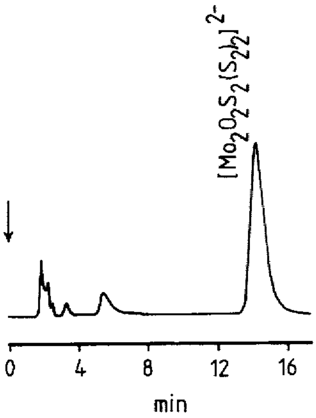


Fig. 8. Separation of $[Mo_2O_2S_2(S_2)_2]^{2-}$. Separator, MPIC-NS 1; eluent, 0.001 M Na_2CO_3 + 0.002 M tetrabutylammonium hydroxide–acetonitrile (50:50, v/v); UV detection at 254 nm; flow-rate, 1 ml/min; solute concentration, 100 mg/l $(NH_4)_2$ $[Mo_2O_2S_2(S_2)_2]$.

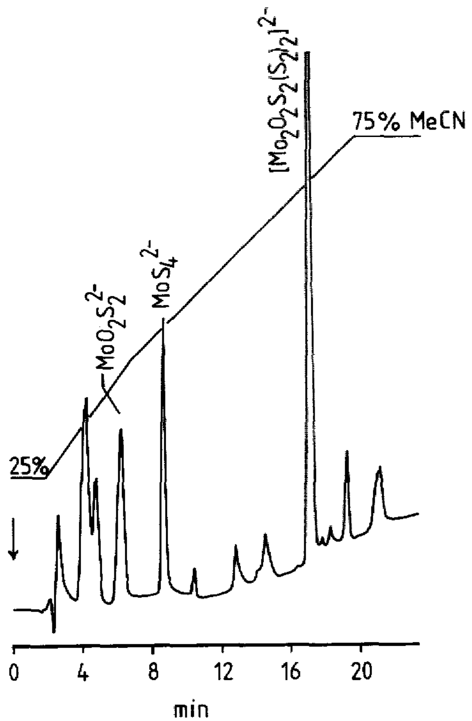


Fig. 9. Gradient analysis of $[Mo_2O_2S_2(S_2)_2]^{2-}$ after hydrolysis of $MoO_2S_2^{2-}$. Separator, MPIC-NS 1; eluent, (A) 0.001 *M* Na_2CO_3 + 0.002 *M* tetrabutylammonium hydroxide–acetonitrile (75:25, v/v), (B) 0.001 *M* Na_2Co_3 + 0.002 *M* tetrabutylammonium hydroxide–acetonitrile (25:75, v/v); UV detection at 254 nm; flow-rate, 1 ml/min; reaction mixture diluted 1:10.

Utilizing gradient elution, the original reaction product was analysed for its constituents. Fig. 9 shows the chromatogram of the 10-fold diluted reaction mixture [1.8 g of $(NH_4)_2MoO_2S_2$ in 25 ml of water], heated at 100°C for 10 min prior to injection. In addition to the starting material and the binuclear reaction product, a significant amount of tetrathiomolybdate could also be identified.

Utilizing MPIC, the formation of $[Mo_2O_2S_2(S_2)_2]^{2-}$ via acidification of an aqueous solution of $MoO_2S_2^{2-}$ could now be verified chromatographically. Treating an aqueous solution containing 500 mg/l of $(NH_4)_2MoO_2S_2$ with 1 *M* hydrochloric acid a fast change of colour from yellow to dark red can be observed. The chromatogram of the 10-fold diluted reaction mixture shown in Fig. 10 clearly demonstrates the formation of the disulphido complex. As a second reaction product $[MoS_9]^{2-}$ was identified, which is more strongly retained than the binuclear poly(thiomolybdate).

Molybdenum sulphur clusters

Another class of complexes containing bridging disulphido ligands, S_2^{2-}, are those with structure II in which the S–S bond is oriented approximately perpendicularly to the metal–metal vector so that each sulphur atom is bonded to both metal atoms[20].

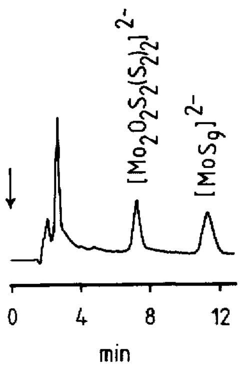
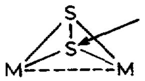


Fig. 10. Analysis of $[Mo_2O_2S_2(S_2)_2]^{2-}$ after acidification of $MoO_2S_2^{2-}$. Separator, MPIC-NS 1; eluent, 0.001 *M* Na_2CO_3 + 0.002 *M* tetrabutylammonium hydroxide–acetonitrile (45:55, v/v); UV detection at 254 nm; flow-rate. 1 ml/min; reaction mixture diluted 1:10.



II

Of particular interest are cluster anions which only contain molybdenum and sulphur. The binuclear cluster $[Mo_2(S_2)_6]^{2-}$ only contains disulphido ligands. Two of the S_2^{2-} ligands are bridging the two molybdenum atoms while four of the S_2^{2-} ligands are bonded to a single molybdenum atom. The trinuclear cluster $[Mo_3S(S_2)_6]^{2-}$ may be regarded as a model for crystalline molybdenum(IV) sulphide[21] (MoS_2 catalysts play an important role in the hydrodesulphurization of pe-

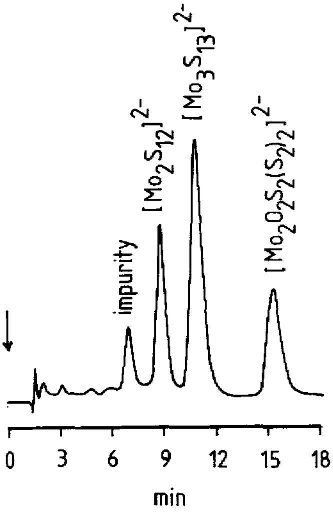


Fig. 11. Separation of various disulphido complexes of molybdenum. Chromatographic conditions as in Fig. 8; solute concentration, 50 mg/l $(NH_4)_2Mo_2S_{12}$ and $[(CH_3)_4N]_2[Mo_2O_2S_2(S_2)_2]$, 100 mg/l $(NH_4)_2[Mo_3S_{13}]$.

troleum). The synthesis of $[Mo_3S(S_2)_6]^{2-}$ (ref. 11) is carried out by treating MoO_4^{2-} with an aqueous polysulphide solution at 90°C, addition of more polysulphide to the filtrate and reduction of the temperature to 30–40°C, yielding under an inert gas $[Mo_2(S_2)_6]^{2-}$ (ref. 11). Both molybdenum–sulphur clusters can be separated by MPIC under the same chromatographic conditions used for $[Mo_2O_2S_2(S_2)_2]^{2-}$. Fig. 11 shows the separation of all three molybdenum–sulphur complexes. The binuclear compound $[Mo_2(S_2)_6]^{2-}$ is the first to elute, followed by the trinuclear cluster[22] and the bisdisulphido complex. Injection of the single components proved $[Mo_2(S_2)_6]^{2-}$ to contain a major impurity that was less retained than the binuclear cluster. The chemical nature of this impurity could not be identified, but the chromatographic behaviour suggests another binuclear compound.

Very little is known about the reactivity of coordinated S_2^{2-} ligands. Müller *et al.*[23] reported a reaction of $[Mo_2(S_2)_6]^{2-}$ with nucleophiles N such as OH^- in an aqueous alkaline medium, yielding $[Mo_2O_2S_2(S_2)_2]^{2-}$. This result clearly demonstrates that bridging S_2^{2-} ligands in $[Mo_2(S_2)_6]^{2-}$ are particularly activated towards reactions with nucleophiles whereas terminal S_2^{2-} ligands are not reactive at all. The degradation of $[Mo_2(S_2)_6]^{2-}$ to the bisdisulphido complex was investigated chromatographically in order to establish the other final products of this reaction. For this purpose 0.65 g of $(NH_4)_2[Mo_2S_{12}]$ was dissolved in 75 ml of 25% ammonia solution. This solution was left for 16 h in contact with air, changing in colour from dark brown to orange. Fig. 12 shows the chromatogram of the 10-fold diluted re-

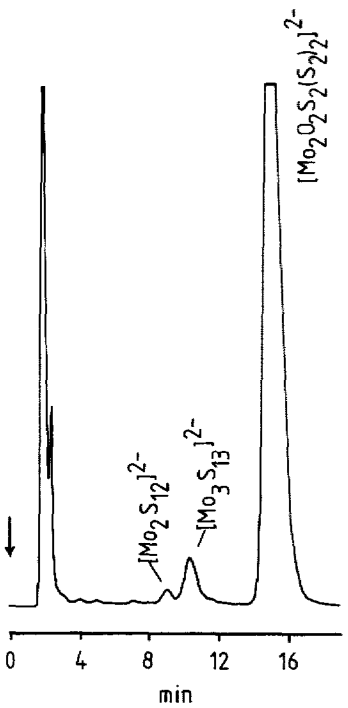
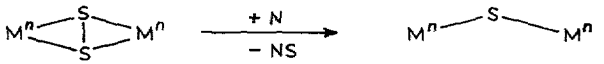


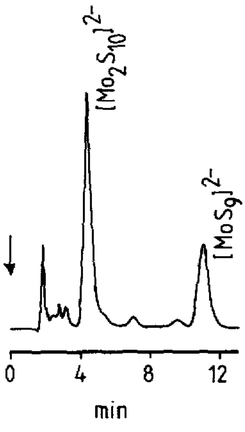
Fig. 12. Analysis of $[Mo_2O_2S_2(S_2)_2]^{2-}$ after hydrolysis of $[Mo_2S_{12}]^{2-}$. Chromatographic conditions as in Fig. 8; reaction mixture diluted 1:10.

action mixture. In addition to $[Mo_2O_2S_2(S_2)_2]^{2-}$ as the major reaction product, some $[Mo_3S_{13}]^{2-}$ could be identified as a side-product. The chromatogram in Fig. 12 clearly demonstrates the utility of ion-pair chromatography for the investigation of this degradation reaction. $[Mo_2S_{10}]^{2-}$, which was suggested as one of the possible intermediates by Müller *et al.*[22], can also be separated under the same chromatographic conditions as used in Figs. 11 and 12. The chromatogram of the respective tetraphenylphosphonium salt is shown in Fig. 13. As expected, $[Mo_2S_{10}]^{2-}$ is significantly less retained than $[Mo_2S_{12}]^{2-}$. The lower retention of $[Mo_2S_{10}]^{2-}$ in comparison with that of $[Mo_2S_{12}]^{2-}$ can be attributed to the abstraction of neutral sulphur atoms from the $[Mo_2S_{12}]^{2-}$ complex (reaction 8), which, in turn, decreases the solvophobic surface area of the solute ion pair.



(in $[Mo_2S_{12}]^{2-}$) (in $[Mo_2S_{10}]^{2-}$) (8)

In contrast to the binuclear compound $[Mo_2S_{10}]^{2-}$, the mononuclear $[MoS_9]^{2-}$ exhibits a much higher retention. Both compounds are obtained under similar experimental conditions (see Experimental), adding elemental sulphur to MoS_4^{2-} in an organic solvent at different temperatures. Fig. 14 shows a chromatogram of $[MoS_9]^{2-}$ precipitated as the tetraphenylphosphonium salt at 5–7°C, indicating that $[Mo_2S_{10}]^{2-}$ has also been formed in a much higher concentration. To elute the strongly retained $[MoS_9]^{2-}$ in a reasonable time, the amount of acetonitrile added to the aqueous mobile phase had to be slightly increased.



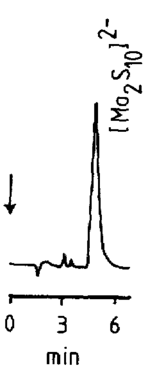
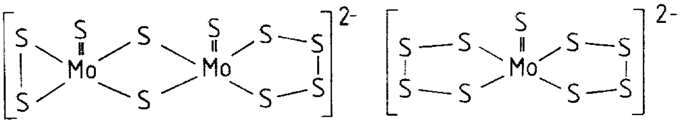


Fig. 13. Separation of $[Mo_2S_{10}]^{2-}$. Chromatographic conditions as in Fig. 8; solute concentration, 100 mg/l $(PPh_4)_2[Mo_2S_{10}]$.

Fig. 14. Separation of $[MoS_9]^{2-}$. Chromatographic conditions as in Fig. 10; solute concentration, 100 mg/l $(PPh_4)_2[MoS_9]$.

The unusually high retention of $[MoS_9]^{2-}$ in comparison with that of $[Mo_2S_{10}]^{2-}$ can be attributed to the differences in structure[24], *viz.*,



An Mo–S arrangement represents a local polar centre which permits an increased interaction with the polar eluent via solvation. Each such group will decrease the retention, depending on the water content of the eluent. With $[Mo_2S_{10}]^{2-}$, the bridging sulphido groups will not contribute to retention at all, while the retention contribution of the disulphido and tetrasulphido ligands is partly compensated by the local polar centres around the molybdenum atoms. With $[MoS_9]^{2-}$ the retention contribution of the doubly bonded sulphur is negligible for the same reason. The two tetrasulphido ligands, on the other hand, are subject to solvophobic expulsion, thus leading to enhanced retention.

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