Preparation of Tetramethylammonium Selenosulfate. Infrared and Raman Spectra of Tetramethylammonium Selenosulfate and Thiosulfate

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Selenium-free tetramethylammonium selenosulfate in high yield can be prepared easily from the corresponding sulfite and elemental selenium in methanol. Tetramethylammonium selenosulfate, like the corresponding thiosulfate, is rather soluble in warm methanol, only limitedly soluble in ethanol and appears insoluble in both acetone and acetonitrile.

The selenosulfate ion acts as an electrophile and thus as a selenating agent toward both triphenylphosphine and ionic cyanide, but only in solvents in which the tetramethylammonium salt is soluble. Toward alkyl halides the selenosulfate ion is a powerful nucleophile and the facile preparation of some tetramethylammonium "seleno-Bunte" salts, $Me_4N^+RSeSO_3^-$, is described.

The infrared and Raman spectra of tetramethylammonium selenosulfate and thiosulfate together with the assigned fundamentals are presented. As anticipated, the selenosulfate ion probably possesses the thionic structure with C_{3v} symmetry similar to that of the thiosulfate ion.

In an aqueous solution of a metal sulfite, preferably the very soluble potassium salt, elemental selenium readily dissolves, particularly at elevated temperatures [1-5] and the following equilibrium is established:

$$SO_3^{2-} + Se(s) \rightleftharpoons SeSO_3^{2-} \qquad (1)$$
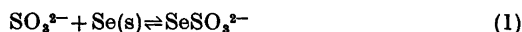
Due to the positive temperature dependence of the equilibrium constant for eqn. 1,[6] salts of the selenosulfate ion have been most difficult to obtain in pure form since selenium will precipitate along with the desired selenosulfate upon cooling of the reaction mixture. The first selenosulfate, K_2SeSO_3, was prepared by

Rathke,[7] but his synthetic route led to an impure product.[8] As shown by Janickis and co-workers,[9] potassium selenosulfate can be stored for years when properly purified.

SYNTHESIS OF TETRAMETHYL-AMMONIUM SELENOSULFATE

We have looked for improved synthetic routes for the preparation of pure salts of the selenosulfate ion. An attempt to use the reaction of elemental selenium with tetramethylammonium sulfite or tetraphenylarsonium sulfite in acetonitrile failed. The product of the reaction was not the expected selenosulfate, but the diselenotetrathionate,[10] although oxygen was carefully excluded during the reaction:

$$SO_3^{2-} + Se(s) \xrightarrow{\text{MeCN}} {}^-O_3SSeSeSO_3^- \qquad (2)$$
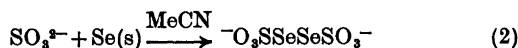
The reaction between onium sulfites and selenium in warm methanol was far more successful. From tetramethylammonium sulfite a selenosulfate of high purity was obtained rapidly in high yield, (usually more than 70 %), eqn. 3:

$$(Me_4N)_2SO_3 + Se(s) \xrightarrow[\text{5 min, 50°C}]{\text{MeOH}} (Me_4N)_2SeSO_3 \qquad (3)$$
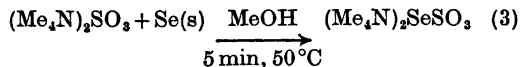
Due to the low solubility of this salt in cold methanol, it crystallized rapidly from the reaction mixture prior to the formation of elemental selenium. Cold ethanol, 0 °C, was
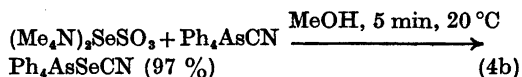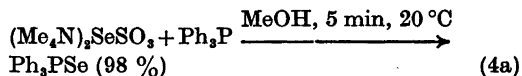
used to remove from the crystalline product unreacted tetramethylammonium sulfite and sulfate, the latter compound formed by possible oxidation of the sulfite. (Separate experiments showed that both these two salts are soluble in cold ethanol.) When tetraphenylarsonium sulfite was employed, the corresponding selenium-free selenosulfate was rapidly obtained in a similar way. However, pure samples of tetraphenylarsonium selenosulfate could not be obtained since the solubility of this salt does not allow the product to be washed with any of the usual protic and aprotic solvents to remove unreacted tetraphenylarsonium sulfite and possibly sulfate.

Tetramethylammonium selenosulfate is a colourless crystalline compound which decomposes slowly in moist air, but can be stored for months without decomposition when stored in a closed bottle. When dissolved in methanol, water or warm ethanol, the equilibrium according to eqn. 1 is set up immediately and red selenium is precipitated. As in aqueous solution, the temperature coefficient of the equilibrium constant in methanol, eqn. 1, is positive, but the large difference in solubility of tetramethylammonium selenosulfate in methanol at 50 °C and at room temperature is the probable cause for the facile formation of the selenium-free selenosulfate. At 25 °C, some 30 % of a 0.02 M solution of tetramethylammonium selenosulfate in methanol is decomposed, a little less than in distilled water of pH 6.0. At 50 °C considerably less is decomposed in methanol, allowing the salt to be crystallized from this solvent without extensive losses. (See Experimental Part.) In refluxing acetone and acetonitrile, tetramethylammonium selenosulfate appears quite insoluble. No selenium was precipitated during the attempt to dissolve the salt in these two solvents, but in acetonitrile the solution turned very slowly yellow, presumably due to traces of tetramethylammonium diselenotetrathionate, according to eqn. 2.

REACTIONS

Tetramethylammonium selenosulfate as electrophilic agent (selenating agent). Tetramethylammonium selenosulfate is deselenated quantitatively and very rapidly by both triphenyl-

phosphine and ionic cyanide in methanol according to eqns. 4a and 4b:

$$(Me_4N)_2SeSO_3 + Ph_3P \xrightarrow{\text{MeOH, 5 min, 20 °C}}$$
$$Ph_3PSe \ (98 \ \%) \tag{4a}$$

$$(Me_4N)_2SeSO_3 + Ph_4AsCN \xrightarrow{\text{MeOH, 5 min, 20 °C}}$$
$$Ph_4AsSeCN \ (97 \ \%) \tag{4b}$$

The latter reaction provides a simple test of the purity of the compound by measuring the amount of ionic selenocyanate, $SeCN^-$, formed, by recording the IR spectrum,[11] after transfer of the reaction mixture to acetonitrile.

In acetonitrile and in acetone, no yield of triphenylphosphine selenide, eqn. 4a, could be obtained, and the formation of ionic selenocyanate, eqn. 4b, was exceedingly slow, presumably due to the negligible solubility of the salt in these solvents. Tetramethylammonium selenosulfate can thus only be applied as a selenating agent in a solvent in which it is soluble. Tetramethylammonium thiosulfate could similarly only form ionic thiocyanate with ionic cyanide in protic solvents. (See Experimental Part.)

Tetramethylammonium selenosulfate as nucleophilic agent. Formation of "seleno-Bunte" salts from alkyl iodides, RI. Tetramethylammonium selenosulfate dissolves without decomposition in methanolic solutions of methyl iodide and 4-nitrobenzyl iodide, forming very rapidly the corresponding Se-alkyl selenosulfates, "seleno-Bunte" salts, in high yield according to eqn. 5:

$$(Me_4N)_2SeSO_3 + RI \xrightarrow[-Me_4NI]{\text{MeOH}} Me_4NRSeSO_3 \tag{5}$$
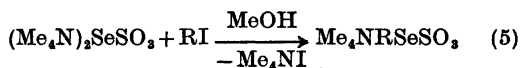
The organic iodides are favourable compared to the bromides and the chlorides since, due to their higher reactivity, their reaction with the selenosulfate ion takes place during the mixing of the reagents preventing the decomposition of the selenosulfate ion to take place according to eqn. 1. Furthermore, the very limited solubility of tetramethylammonium iodide in methanol allows this product from the reaction to be easily removed from the reaction mixture.

A number of well-characterized "seleno-Bunte" salts have previously been prepared

from the selenosulfate ion, made *in situ* according to eqn. 1, and alkyl and activated aryl iodides.[12–16] However, since the decomposition of organic selenosulfates is known to be catalyzed by both acid, base and heat,[16–18] pure tetramethylammonium selenosulfate in methanol appears superior to potassium selenosulfate prepared *in situ* for the synthesis of "seleno-Bunte" salts.

The readiness by which the reaction between tetramethylammonium selenosulfate and alkyl iodides takes place clearly indicates that the selenosulfate ion is a very powerful nucleophile. This is not surprising in view of the fact that the selenosulfate ion is very easily oxidized.[1,19–21] The high yield of "seleno-Bunte" salts from alkyl halides and potassium selenosulfate, prepared *in situ*,[12–16] suggests that the sulfite ions present cannot compete with the selenosulfate ions for the organic substrate. Since

the thiosulfate ion is only three times as reactive as the sulfite ion toward methyl iodide in methanol,[21] it is conceivable that the selenosulfate ion is more nucleophilic than is the thiosulfate ion, a conclusion which fits nicely into the generally accepted pattern of the relative nucleophilicity of divalent selenium and sulfur species toward polarizable substrates: $NCSe^- > NCS^-$, $R_2Se > R_2S$, $PhSe^- > PhS^-$, $O_3SSe^{2-} > O_3SS^{2-}$.[21]

SPECTROSCOPIC STUDIES

Tetramethylammonium thiosulfate was prepared in approximately the same way as the corresponding selenosulfate (see Experimental Part). Therefore, non-hygroscopic salts of these two ions without crystal water or small polarizing cations were available for the spectroscopic study. Accordingly, the spectra of these com-

Table 1. Infrared and Raman spectral data for tetramethylammonium thiosulfate below 1200 cm^{-1}.[a]

Infrared Nujol	KBr	Raman Solid	Interpretation
1195 vw		1197 w	$N(CH_3)_4^+$
1168 vw	1176 m		$N(CH_3)_4^+$
1160 w ⎫	1160 m ⎫		
1132 vs ⎬	1140 vs ⎬	1124 m	ν_4, E
1118 s ⎭	1125 s ⎭		
1092 w			
1050 vw	1048 w		
1020 w	1024 m	1033 w	
	1007 s ⎫		
996 s	998 s ⎬	996 m	ν_1, A_1
960 m ⎫	951 s ⎫		
950 s ⎬	945 s ⎬	955 m	$N(CH_3)_4^+$
918 w	918 w		$N(CH_3)_4^+$
866 vw			
845 w			
		757 s	$N(CH_3)_4^+$
665 w ⎫	674 s ⎫		
653 s ⎬	677 s ⎬	653 vs	ν_2, A_1
640 w ⎭	657 s ⎭		
610 w	616 w		
	547 m ⎫		
533 m	538 m ⎬	537 w	ν_5, E
	536 m ⎭		
462 m	454 w	460 s	$N(CH_3)_4^+$
435 vw	431 vw	436 vs	ν_3, A_1
370 vw	370 w[b]	378 w	
331 vw	335 w[b] ⎫	322 s	ν_6, E
	324 w[b] ⎭	190 vw	
		95 vs	lattice

[a] Abbreviations: s, strong; m, medium; w, weak and v, very. [b] Polyethylene (Rigidex) pellet.

Table 2. Infrared and Raman spectral data for tetramethylammonium selenosulfate below 1200 cm⁻¹.ᵃ

Infrared Nujol	KBr	Raman Solid	Interpretation
	1191 m	1198 vw	$N(CH_3)_4^+$
	1150 s ⎫	1139 vw	ν_4, E
1140 vs	1128 vs ⎭		
1091 vw			
	1051 w		
1041 m	1042 m	1032 m, br	
1019 s ⎫	1011 s, sh ⎫		
	1004 s ⎬	994 m	ν_1, A_1
996 vs ⎭	996 s ⎭		
959 s ⎫	950 s ⎫	954 w	$N(CH_3)_4^+$
949 s ⎭	944 s ⎭		$N(CH_3)_4^+$
921 w	917 w		
845 w		754 s	$N(CH_3)_4^+$
650 w ⎫	652 s ⎫	639 s	ν_2, A_1
638 vs ⎬	644 s ⎭		
616 m ⎭			
	595 m		
540 m ⎫	550 w ⎫	528 vw, br	ν_5, E
538 w ⎬	530 w, sh ⎬		
522 m ⎭	526 m ⎭		
462 m	454 w	457 m	$N(CH_3)_4^+$
302 vw	300 wᵇ	300 vs	ν_3, A_1
281 vw	278 wᵇ	277 s	ν_6, E
	250 vwᵇ	242 w	
	225 vwᵇ	227 w	
		205 vw	
		117 w	
		88 s	lattice

ᵃ Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder and br, broad. ᵇ Polyethylene (Rigidex) pellet.

Table 3. Fundamental frequencies ᵃ for the thiosulfate and the selenosulfate ions in their tetramethylammonium salts.

$S_2O_3^{2-}$	$SeSO_3^{2-}$	No.	Species	Assignment
996	996	ν_1	A_1	S — O stretch
653	638	ν_2	A_1	S — O bend
436ᵇ	300ᵇ	ν_3	A_1	S — S (S — Se) stretch
1132	1140	ν_4	E	S — O stretch
533	522	ν_5	E	S — O bend
322ᵇ	277ᵇ	ν_6	E	SO_3 rock

ᵃ Infrared bands from the nujol spectra, except when noted. ᵇ Bands observed in the Raman spectra.

pounds are to a good approximation expected to give a superposition of the cation $N(CH_3)_4^+$ and the anion SSO_3^{2-} or $SeSO_3^{2-}$ spectra. The thiosulfate ion has been investigated in a number of compounds by X-ray [22–25] and spectroscopic [26–29] methods and is known to belong to point group C_{3v}.[30]

The observed infrared and Raman lines below 1200 cm⁻¹ for tetramethylammonium thiosulfate and selenosulfate, respectively, are

listed in Tables 1 and 2. Tentative interpretations of the major infrared and Raman lines are presented. As apparent, a number of the observed bands can with reasonable confidence be attributed to the cation $N(CH_3)_4^+$ since they are present in a number of salts containing this ion.[31-33] More interesting for the present work are the bands attributed to the anions, and in Table 3 the fundamentals assigned to the thiosulfate and the selenosulfate groups are listed. The thiosulfate modes agree well with the results of earlier work.[26-28] With C_{3v} symmetry the fundamentals divide themselves between the symmetry species 3 A_1 and 3 E. Since no Raman polarization ratios can be obtained from the solid state spectra, the A_1 and E fundamentals cannot be distinguished with certainty. In most cases the A_1 modes give rise to the most intense Raman bands in the spectra. Also, the degenerate S − O stretch (E) will generally be at higher frequencies than the totally symmetric ones (A_1) while the opposite will be the case for the S − O bending modes.

In the selenosulfate ion we have no guide-lines from previous work. Particularly, the molecular structure of this ion is unknown, but an X-ray crystallographic determination of tetramethylammonium selenosulfate is presently being carried out. As apparent from Table 3 the various vibrations ν_1, ν_2, ν_4 and ν_5 are only slightly displaced from the thiosulfate to the selenosulfate ions. This fact strongly suggests C_{3v} molecular symmetry also in the selenosulfate group, since lower symmetry (e.g. C_s) would lead to splitting of the doubly degenerate E modes contrary to the observations (Tables 1 and 2). More definite conclusions regarding the structure could be extracted from the spectra only when Raman polarization data become available. The lowest A_1 fundamental involving mainly S − Se stretch was assigned to the very intense Raman band at 300 cm^{-1} having weak counterparts in the infrared. This value agrees with the suggested S − Se stretching frequency in the selenopentathionate ion.[35]

The shift of the S − Se stretch (436) compared to the S − S stretch (300 cm^{-1}) is much larger than caused by the increased atomic mass of the atom, only. A considerable weakening of the S − Se force constant (compared to S − S) is in agreement with the chemical experience of the weak S − Se bond in the selenosulfate ion. Finally, the lowest E fundamental is attributed to the intense Raman band at 277 cm^{-1} with weak IR counterparts. Again, the large shift from the thiosulfate ion frequency at 322 cm^{-1} is not surprising because of the increased mass and weaker S − Se bond compared with the S − S bond.

The conclusion arrived at in the present study with regard to the structure of the selenosulfate ion conforms with results from recent infrared spectra of sodium and potassium selenosulfate.[36,37] The selenosulfate complexes, $Zn(en)_2SeSO_3$ and $Cu(en)_2SeSO_3$, (en = ethylenediamine), have been shown by X-ray methods to be isostructural with the corresponding thiosulfate complexes.[38-40]

EXPERIMENTAL

Solvents: Merck's *Methanol zur Analyse* was used without further purification since separate experiments showed that the decomposition of tetramethylammonium selenosulfate in this solvent according to eqn. 1 was the same as in a solvent batch distilled from magnesium methoxide, $Mg(OCH_3)_2$.

Acetonitrile, *Baker Analyzed Reagent*, was distilled from phosphorus pentaoxide, P_2O_5, and finally from calcium hydride, CaH_2. The solvents applied in the present study were carefully flushed with dry oxygen-free nitrogen.

All operations with solutions of salts of the selenosulfate ion, the thiosulfate ion and the sulfite ion were carefully performed under nitrogen.

Tetramethylammonium sulfite, $(Me_4N)_2SO_3$. To 20.1 g tetramethylammonium iodide, Fluka *purum*, carefully washed with acetonitrile and diethyl ether, in 200 ml methanol was added 14.8 g freshly prepared silver sulfite. The slurry was stirred at room temperature for 3 h, filtered, and stirred for still 1 h after the addition of 1 g of silver sulfite. After filtration and removal of the solvent in vacuum, the product was repeatedly dissolved in methanol and azeotropically dried with benzene to remove traces of water and silver compounds. The final product was slightly greyish suggesting some silver species to be present. All attempts to crystallize the product from the usual protic and aprotic solvents failed. [Yield 10.3 g (90 %)]. An IR spectrum (nujol) showed that the amount of tetramethylammonium sulfate (made in a similar way from silver sulfate) present was negligible. However, an absorption in the 3500 cm^{-1} region suggested the presence of residual water.

Tetramethylammonium selenosulfate, $(Me_4N)_2$ $SeSO_3$. To 10.3 g tetramethylammonium sulfite

dissolved in 100 ml methanol was added an equivalent amount of black selenium powder. No reaction was found to take place at room temperature. However, at reflux temperature nearly all selenium was consumed during 5 min and a slightly yellow solution was obtained. The solution was rapidly filtered and the product immediately separated as white needles (yield 8.9 g). After addition of 100 ml ethanol to the mother liquor, an additional amount of 2.0 g pure salt was obtained. Total yield 10.9 g, 78 %. M.p. 171 °C (dec.). (Found: C 30.82; H 7.36; N 9.51. Calc. for $C_8H_{24}N_2O_3SSe$: C 31.26; H 7.87; N 9.12.) The salt could be recrystallized from methanol at reflux temperature in more than 70 % yield. The melting point and IR spectrum (in the $4000-650$ cm^{-1} region) was unaltered after this purification.

Tetramethylammonium thiosulfate. This salt was made analogous to tetramethylammonium selenosulfate, from tetramethylammonium sulfite and elemental sulfur. However, if sulfur was used in excess or even in an equivalent amount, the product obtained was slightly yellow, a colour which could not be removed by repeated crystallizations from methanol or by washings with carbon disulfide. When tetramethylammonium sulfite was used in 5 % excess, these difficulties were not encountered. Since the solubility of this salt in cold methanol is considerable, the volume was reduced to 50 ml prior to filtration and crystallization. From 10.3 g tetramethylammonium sulfite and 1.2 g sulfur the yield of crude product was 7.8 g. The salt was crystallized from 50 ml methanol yielding 5.4 g pure product, 57 % based upon the added amount of sulfur, m.p. $238-240$ °C. The salt appeared non-hygroscopic. (Found: C 36.48; H 9.15; N 11.34; S 24.92. Calc. for $C_8H_{24}N_2O_3S_2$: C 36.89; H 9.29; N 10.76; S 24.63.)

Decomposition of tetramethylammonium selenosulfate in protic solvents. (1) *Methanol at reflux temperature:* 5.9 g, 0.019 mol, dissolved in 100 ml methanol at reflux temperature, (0.19 M solution), gave 0.253 g, 0.0032 mol, selenium, 17 %. (2) *Methanol at 25 °C:* 0.307 g, 1×10^{-3} mol, dissolved in 50 ml methanol, (0.02 M solution) was stirred at 25 °C for 30 min and filtered. Yield of selenium 0.0281 g, 35 %. (3) *Distilled water, pH 6, at 25 °C:* 0.307 g, 1×10^{-3} mol, dissolved in 50 ml water, (0.02 M solution) was stirred at 25 °C for 30 min and filtered. The precipitated selenium was washed with methanol and finally with ether. Yield of selenium 0.0333 g, 42 %.

Reactions of tetramethylammonium selenosulfate. 1. *Ionic cyanide.* To 10 ml 0.02 M solution of tetraphenylarsonium cyanide in methanol was added 0.0163 g tetramethylammonium selenosulfate. The salt dissolved immediately with no formation of selenium. The solution was evaporated to dryness, dissolved in acetonitrile and the amount of tetraphenylarsonium selenocyanate, $Ph_4AsSeCN$, formed determined

by liquid IR. Found: 97 ± 2 %. Similar experiments employing 0.0142 g tetramethylammonium thiosulfate gave 97 ± 2 % of the theoretical amount of ionic thiocyanate, SCN$^-$. When these experiments were performed in acetonitrile, less than 5 % ionic selenocyanate and thiocyanate could be detected after 1 h.

2. *Triphenylphosphine.* To 0.524 g triphenylphosphine, Ph_3P, 2×10^{-3} mol, dissolved in 20 ml methanol was added an equivalent amount of tetramethylammonium selenosulfate, 0.614 g. The salt dissolved immediately without formation of selenium. The reaction mixture was stirred for 15 min at room temperature whereupon triphenylphosphine selenide, Ph_3PSe, started to separate. After 12 h in the refrigerator 0.670 g triphenylphosphine selenide, m.p. $187-188$ °C, $(189 °C^{41})$ was obtained, 98 %. In ethanol, 5 min at reflux temperature was necessary to obtain a quantitative yield of triphenylphosphine selenide. In acetonitrile, no yield of triphenylphosphine selenide could be detected after 24 h at room temperature.

3. *Alkyl iodides, RI.* To 4×10^{-3} mol of the alkyl iodide, RI, in 25 ml methanol was added an equivalent amount of tetramethylammonium selenosulfate. The salt dissolved immediately with only slight reddish colouration of the reaction mixture which disappeared after a few minutes. After 5 min at room temperature all ionic selenosulfate was consumed (no colour due to elemental selenium was observed when 1 ml of the reaction mixture was added to 10 ml of water). The reaction mixture, turbid due to precipitated tetramethylammonium iodide, was set aside for 2 h in the refrigerator and then filtered. The mother liquor was three times dissolved in a minimum amount of methanol, cooled and filtered to ensure a complete removal of tetramethylammonium iodide. The salts were finally recrystallized from acetonitrile, if necessary with some diethyl ether added.

$R = Me$: White microcrystalline compound with obnoxious odour which could not be removed by repeated purifications. The salt appears hygroscopic, yield 54 %. M.p. (acetonitrile/diethyl ether): 171 °C (dec.). (Found: C 24.29; H 5.96; N 5.44. Calc. for $C_5H_{14}NO_3SSe$: C 24.19; H 6.09; N 5.64.)

$R = 4$-*Nitro-benzyl*, $NO_2-C_6H_4-CH_2$: Slightly yellowish compound, m.p. (acetonitrile) $175-177$ °C (dec.). 74 % yield. (Found: C 35.30; H 5.37; N 7.64. Calc. for $C_{11}H_{18}N_2O_5SSe$: C 35.77; H 4.92; N 7.59.)

Instrumental. The IR spectra were recorded with Perkin-Elmer model 225 ($1400-200$ cm^{-1}) and 180 ($1400-180$ cm^{-1}) spectrometers. The solid samples were investigated in KBr pellets CsI and polyethylene (Rigidex) pellets, and Nujol mulls between CsI plates.

A Coderg model T 800 triple monochromator spectrometer equipped with a Spectra Physics model $170-03$ argon ion laser was employed for the Raman recordings, using the 5145 Å

line for excitation. The samples were filled into capillary tubes and recorded with *ca.* 80 mW power after the plasma lines were removed with an interference filter. Improved spectra were recorded with the aid of a spinning sample holder (Coderg) permitting the use of 250 mW laser power. Most of the Raman spectra were recorded with spectral slit widths of *ca* $2-3$ cm^{-1}.

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