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Taming the Oxidative Power of SeO_3 in 1,4-Dioxane, Isolation of Two New Isomers of Mixed-Valence Selenium Oxides, and Two Unprecedented Cyclic Esters of Selenic Acid

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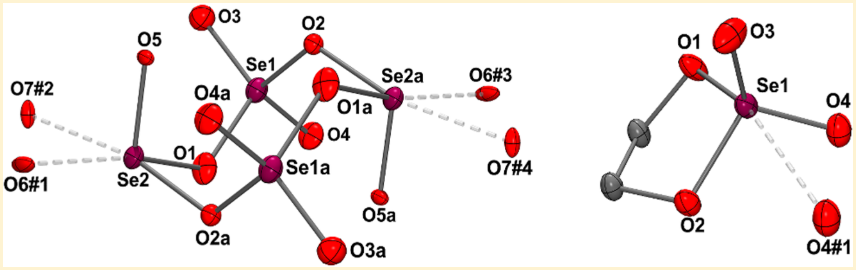
Supporting Information



ABSTRACT: The reaction of $(SeO_3)_4$ with 1,4-dioxane (diox, dioxane) with or without diluting solvent led to the isolation of the unprecedented esters of selenic acid-1,2-ethyl selenate $(CH_2O)_2SeO_2$ and the glyoxal diselenate $O_2Se[(OCHO)_2]SeO_2$. It was possible to isolate an unknown dimeric form of Se_2O_5 $(Se_4O_{10}\cdot(diox)_2)$ and a geometrical isomer of the mixed-valence oxide *trans*-Se_3O_7, both stabilized by dioxane. The dioxane adduct of monomeric selenium trioxide $SeO_3\cdot diox$ was obtained from the reaction of $(SeO_3)_4$ with dioxane in liquid SO_2. The reaction mechanism for the formation of these compounds was elucidated, and the molecular structure of the unstable form of the selenium trioxide was determined, consisting in a trimeric arrangement $(SeO_3)_3$.

■ INTRODUCTION

Selenium is an essential element not only for humans but also for animals and various plants. However, in larger concentrations it is highly toxic to almost any organism. Besides its toxicity, selenium compounds with oxidation state VI are also strong oxidizers, and in fact, species with Se^{VI} and especially SeO_3 are quite unstable in the presence of organic compounds; any such combination results, in the best case, in a cascade of redox reactions albeit in most cases in violent explosions. This behavior contrasts with the mild oxidation properties of SeO_2 used in the Riley oxidation[1] or that of the lighter congener SO_3, which is used as an oxidizing agent in the catalytic process[2] for the oxidation of methane. Also, several organic compounds with sulfur in oxidation state VI such as dimethyl sulfate or 1,2-ethylene sulfate are sold as alkylating agents. Until now, the only compounds combining Se^{VI} with organic groups in one molecule are amino or heavy metals salts of SeO_4^{2-} anions,[3] a few alkyl or aryl selenonates,[4] one example of a $[O_3SeOCH_2OSeO_3]^{2-}$ anion (whose formation could not be explained),[5] and the dimethyl and diethyl ether adducts of SeO_3, reported recently by our group.[6] The reaction of selenium trioxide with 1,4-dioxane (diox, dioxane) without the presence of an inert solvent has been investigated in the past by Schmidt and Wilhelm[7] who assumed that the product isolated at ambient temperature was the adduct $SeO_3\cdot diox$. However, the molecular structure of the product was not confirmed, and on the basis of current knowledge about this reaction system, it is safe to say that the isolated compound contains both Se^{IV} and Se^{VI} centers. This assumption is based on the fact that the acyclic ethers adducts $SeO_3\cdot OEt_2$ and $SeO_3\cdot(OMe_2)_2$ decompose within a few days in solid state or rapidly above their melting points (−9 and 5 °C, respectively) or in solution.[6] Furthermore, the Raman spectra of both ether adducts $SeO_3\cdot OEt_2$ and $SeO_3\cdot(OMe_2)_2$ contain a characteristic intense vibration assigned to the symmetric stretching vibration of monomeric SeO_3 unit at 879 and 881 cm^{-1}, respectively. No such vibration was observed for the product in the original study.[7] Thus, based on our success in the stabilization of the ether adducts of monomeric SeO_3, we decided to reinvestigate the SeO_3/dioxane system, identify the compound prepared in the original report, and try to isolate the $SeO_3\cdot diox$ adduct. Herein, we describe the reaction of pulverized SeO_3 with dioxane resulting in the formation

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of unprecedented examples of cyclic organic esters of selenic acid; 1,2-ethylene selenate, glyoxal diselenate, a new cyclic selenium oxide Se_4O_{10} stabilized by coordinating dioxane, and the *trans* isomer of Se_3O_7. Finally, analytically pure SeO_3·diox adduct, which is stable for a short period of time under an inert atmosphere even at ambient temperature, was prepared from a mixture of dioxane and SeO_3 in liquid sulfur dioxide. Several other reaction intermediates or subproducts were identified in the reaction mixtures and helped to elucidate the mechanism of the formation of the above-mentioned compounds. During the preparation of the selenium trioxide it was also possible to determine the crystal structure, melting point, and the Raman spectrum of the unstable cyclic trimeric form $(SeO_3)_3$, which spontaneously transforms even in the solid state into the well-known tetrameric modification $(SeO_3)_4$.

■ EXPERIMENTAL SECTION

***Caution!** All reactions reported in this paper, including the preparation of SeO_3, feature a high risk of explosion and thus proper precautions should be taken. Thus, all reactions were made behind a blast shield, and if a formation of a yellowish color (caused by traces of elemental selenium from uncontrolled redox reactions) was observed during the reaction, the students retracted to a safe distance immediately. In some cases, it was possible to stabilize such reaction by cooling it below the melting point of the solvent, but if the color of the reaction changed to deep yellow or even orange color (caused by higher concentration of elemental selenium) an explosion occurred within seconds. The only possibility to prevent the explosion is rapid hydrolysis of the reaction by a strong stream of water from a washing bottle. However, it is safer to drop the reaction vessel in a metal container and let the reaction finish (or explode) in a contained environment. All residues were hydrolyzed and disposed as heavy metal acidic waste.*

All reactions were performed in Schlenk flasks or Schlenk tubes with Teflon valves dried at 150 °C for at least 24 h. The solvents were added by oven-dried glass pipet or vacuum-transferred. Sulfur dioxide 99.98% was purchased from Linde, dried by passing through concentrated sulfuric acid and phosphorus pentoxide, and condensed in a sealed tube with P_4O_{10}. Finally, it was vacuum-transferred directly from the P_4O_{10} into a clean, thoroughly dried sealed tube with a Teflon valve. Selenium trioxide was prepared by dehydration of anhydrous selenic acid over P_4O_{10}.[8] Anhydrous selenic acid (20 mL) was distributed evenly over P_4O_{10} (60 g) in a large grease-free sublimation apparatus. After 4 h, the sublimation was started, and crude SeO_3 sublimed at 160 °C in a dynamic vacuum. The crude product was slowly resublimed at 120 °C. Pure SeO_3 is highly hygroscopic; thus, it should be always sublimed prior to use, and also special care should be taken while drying and purifying the solvents. Therefore, dioxane, CCl_4, and nitromethane were purchased from Aldrich (p.a. grade) and purified and dried according to following procedures. Nitromethane was stored for 2 d with occasional shaking over concentrated sulfuric acid (150 mL per 1 L of nitromethane). After decantation, the solvent was washed first with water, then with a solution of sodium carbonate, and finally again with water. Subsequently, the solvent was stored for several days over calcium chloride and distilled. The distillate was refluxed for 1−2 h with calcium hydride, and finally, it was distilled again and stored over 4 Å molecular sieves in the dark. Tetrachloromethane was stored for 2−3 d over phosphorus pentoxide with occasional agitation. After decantation, the tetrachloromethane was distilled and stored over 4 Å molecular sieves. Dioxane was kept 1 d over potassium hydroxide. Subsequently, the solution was decanted over sodium wire and distilled. The distillate was refluxed for 2 h with calcium hydride and distilled over fresh sodium wire.

As any solution of compounds **1**−**5** in organic solvents can explode without any initiation even at low temperature, only Raman spectroscopy (close to liquid nitrogen temperature) and X-ray diffraction studies at −150 °C could be used for their characterization. The Raman spectra were measured on a Bruker Equinox spectrometer equipped with a Raman FRA 106/S module using Nd:YAG laser source (λ = 1064 nm, W = 350 mW). The samples were filled in a 1, 4, or 8 mm nonfluorescent glass capillaries or were measured directly in Schlenk tubes. The band of the SeO_3 unit coordinated by dioxane is an order of magnitude more intense than the rest of the lines, and thus the scale of 1−100 (in brackets after the wavenumber) is used to describe precisely the relative intensities instead of the standard vs, s, m, w, vw scale.

Preparation of Se_4O_{10}·(diox)$_2$ (1). Nitromethane (75 mL) was condensed over SeO_3 (0.391 g, 3.08 mmol) using liquid nitrogen bath. The reaction mixture was warmed to 0 °C under vigorous stirring, and once a clear solution was formed, it was cooled to −10 °C. At this temperature, an equimolar amount of dioxane (0.27 mL, 3.17 mmol) was added under vigorous stirring, and the clear solution changed to turbid. The remaining suspension was kept without stirring for two weeks at −30 °C. Compound **1** was isolated in 30% yield by decantation and evaporation of the remaining solvents under vacuum. Exposing **1** to temperatures over 15 °C or any attempt to recrystallize it led to its decomposition. Raman spectrum: $\tilde{\nu}$ (int) 109 (33), 128 (46), 135 (39), 177 (59), 204 (43), 278 (33), 331 (31), 393 (15), 408 (25), 473 (31), 594 (6), 716 (5), 826 (53), 849 (10), 876 (6), 926 (100), 987 (34), 994 (80), 1012 (34), 1039 (5), 1089 (6), 1129 (15), 1221 (10), 1298 (6), 1308 (16), 1338 (5), 1376 (5), 1446 (16), 1460 (12), 2670 (2), 2723 (3), 2744 (3), 2782 (3), 2867 (7), 2875 (8), 2900 (10), 2919 (11), 2933 (15), 2948 (12), 2986 (22), 2996 (14), 3013 (17) cm^{-1}.

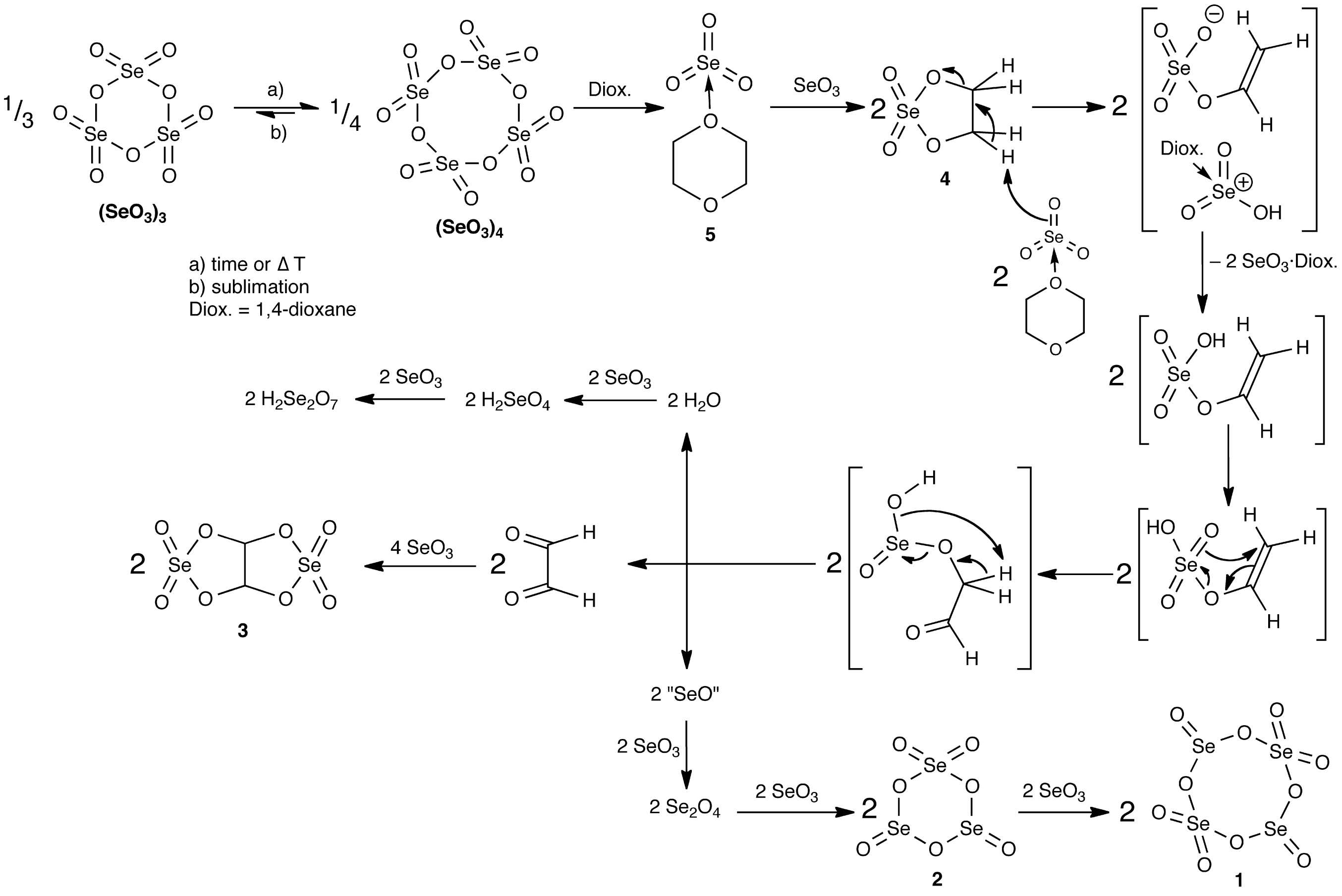
Preparation of Se_3O_7·(diox)$_2$ (2). Finely pulverized SeO_3 (1.104 g, 8.70 mmol) in a Schlenk flask was placed in a bath of liquid nitrogen, and tetrachloromethane (14 mL) was added. After it solidified, dioxane (24 mL) was added at such a rate that it solidified during the addition. The reaction mixture was allowed to warm over the period of 20 min (all SeO_3 should be dissolved after this time) to ambient temperature, and when possible it was vigorously stirred. It is crucial that during the warming of the reaction mixture, there is always solid dioxane if solid SeO_3 is present. Thus, if the dioxane melted before all SeO_3 was dissolved, the reaction was again cooled until it solidified, and the warming process was repeated. **The presence of undissolved SeO_3 in dioxane at ambient temperature resulted in almost all cases in violent explosion!** Subsequently, the solution was concentrated to one-third of its volume and stored without stirring for 3 d at ambient temperature, during which time compound **2** crystallizes in a form of well-defined crystals. Compound **2** is isolated by filtration and drying in vacuum in 80% yield. Raman spectrum: $\tilde{\nu}$ (int) 113 (22), 147 (29), 181 (58), 212 (10), 234 (9), 258 (5), 281 (14), 323 (33), 337 (28), 394b (9), 426 (3), 447 (14), 460 (5), 484 (17), 548b (11), 568sh (5), 819 (50), 824 (69), 847 (10), 852 (8), 921 (75), 958 (36), 987 (100), 1011 (30), 1038 (3), 1086 (3), 1125 (13), 1218 (10), 1225 (6), 1295sh (4), 1301sh (5), 1308 (17), 1335 (3), 1374 (5), 1383 (5), 1399 (2), 1443 (19), 1460 (13), 2732 (5), 2737 (6), 2791 (5), 2869 (21), 2895 (20), 2911 (21), 2925 (22), 2971 (21), 2985 (29), 2991sh (26) cm^{-1}.

Preparation of SeO_3·diox (5).

(a) SeO_3 (0.550 g, 4.33 mmol) was placed in a sealed tube with a Teflon valve, and SO_2 (12.7 g) was added by vacuum transfer using a short stainless-steel vacuum line; a clear colorless solution formed. An equimolar amount of dioxane (0.37 mL, 4.34 mmol) was then added in the same way as SO_2. Compound **5** was isolated in a quantitative yield by evaporation of the SO_2. An alternative route to isolate **5** consists in cooling the solution below −10 °C, decantation of SO_2, and evaporation of the remaining solvent. mp 46.5 °C. Raman spectrum: $\tilde{\nu}$ (int) 231 (3), 256 (3), 360 (4), 436 (2), 484 (2), 803 (4), 876 (100), 929 (1), 990b (3), 1009 (5), 1123 (7), 1211 (4), 1305 (3), 1393 (2), 1445 (5), 1449sh (3), 1464 (4), 2723 (1), 2737 (1), 2781 (1), 2871 (3), 2893 (2), 2904sh (3), 2921sh (3), 2933 (3), 3004 (4), 3016sh (3) cm^{-1}.

(b) An experimentally easier but more dangerous synthesis of **5** with slightly lower purity and stability is based on the synthesis of **2**. Finely pulverized SeO_3 (0.395 g, 3.11 mmol) in a Schlenk flask was placed in a bath of liquid nitrogen, and the SeO_3 was

Scheme 1. Preparation of Compounds 1−5[a]



a) time or Δ T
b) sublimation
Diox. = 1,4-dioxane

[a]Including the mechanism of decomposition of compound **4** into glyoxal, "SeO," and water necessary for the formation of compounds **1**−**3**, H_2SeO_4, and $H_2Se_2O_7$ identified in the reaction mixture.

carefully layered with tetrachloromethane (5.0 mL, 51.8 mmol) at such a rate that the solvent froze instantly. Subsequently, dioxane (10.0 mL, 117.3 mmol) was added in the same fashion. The flask was allowed to warm (during at least 20 min) to the melting point of dioxane (11.8 °C) under vigorous stirring (**faster warming results in almost all cases in explosion**). However, it is important to control very strictly the temperature of the reaction so that there is always some part of undissolved dioxane until all SeO_3 has dissolved. Compound **5** was isolated by removing all volatiles (at temperatures below 15 °C) immediately after obtaining a homogeneous solution.

X-ray Structure Determination. Crystals of compounds **1**−**5**, $(SeO_3)_3$ and $(SeO_3)_4$ were suspended in a cold (at least −20 °C) perfluoropolyether. Suitable crystals were picked and mounted in quartz capillaries or on a glass fiber and were rapidly transferred in a stream of cold nitrogen (−150 °C). It is necessary to keep the temperature of the oil and the crystals below −10 °C during the whole procedure to avoid the risk of explosion. Diffraction data were collected with a KUMA KM-4 four-circle diffractometer[9] with the use of Mo $K\alpha$ radiation (λ = 0.710 73 Å). Structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares on F^2[10] using the SHELXLE GUI.[11] The hydrogen atoms of the C−H bonds were placed in idealized positions and refined with U_{iso} tied to the parent atom. The molecular graphics were prepared using GRETEP, POV-RAY, and GIMP.[12]

■ RESULTS AND DISCUSSION

The first problem with the reaction between SeO_3 and neat dioxane is an insufficient kinetic control due to the necessity to work above the melting point of dioxane (11.8 °C). The only possible way to influence the kinetics of the reaction is to finely pulverize the SeO_3 and add the dioxane at low temperature at such a rate that it instantly solidifies. Subsequently, the temperature is raised at such a rate that the reaction heat is used to melt the excess of dioxane. However, this is technically and experimentally challenging, as it needs precise timing and temperature control. Failure to finely pulverize all SeO_3 or control the temperature caused, in the best case, formation of redox species, albeit in many cases a **violent explosion**. The risk of explosion grows exponentially with particle size and reaction temperature. **Thus, all reactions reported herein were made behind a blast shield, and if a formation of a small amount of elemental selenium (the reaction color turned to pale yellow) was observed during the reaction, the students retracted to a safe distance immediately (see the** Experimental Section **for more details).** After all SeO_3 has dissolved and the dioxane melted (in this order), the reaction mixture was stirred for 5 h at ambient temperature, and the precipitated solid was isolated by filtration. This product, which was probably obtained also by Schmidt and Wilhelm,[7] was identified as $Se_4O_{10}\cdot(diox)_2$ (**1**). However, it was always contaminated by various amounts of $Se_3O_7\cdot(diox)_2$ (**2**), $C_2H_2O_8Se_2\cdot(diox)_2$ (**3**), $H_2Se_2O_7\cdot(diox)_2$, and $H_2SeO_4\cdot diox$, as identified by Raman spectroscopy and X-ray diffraction experiments. The desired adduct $SeO_3\cdot diox$ (**5**) was not observed. Elimination of all volatiles from the mother liquor obtained after the filtration gave a colorless glassy solid. Heating this solid to 50 °C in

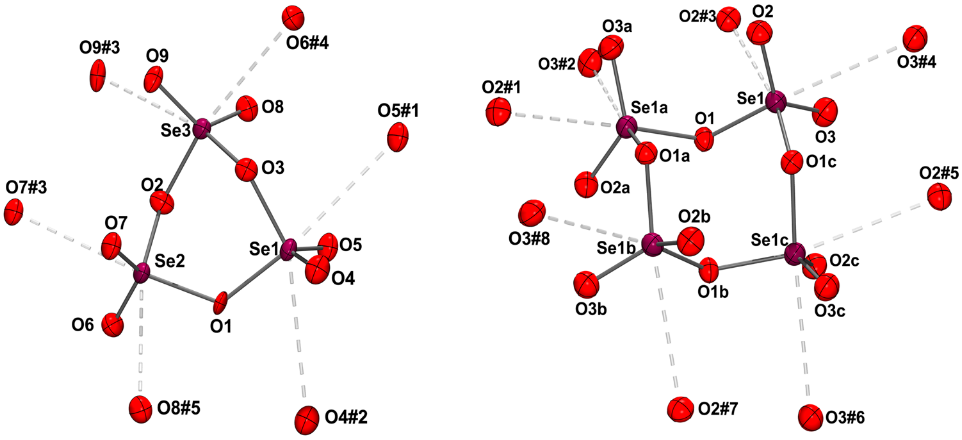


Figure 1. Crystal structures of $(SeO_3)_3$ (left) and $(SeO_3)_4$ with thermal ellipsoids at 50% probability showing close contacts of the selenium atoms to neighboring oxygen atoms. Symmetry codes to generate equivalent atoms for $(SeO_3)_3$ #1: $-x, 1-y, -z$, #2:$1-x, 1-y, -z$, #3: $+x, 3/2-y, 1/2+z$, #4: $-1+x, +y, -1+z$, #5:$1+x, +y, +z$ and for $(SeO_3)_4$ a: $1-y, +x, -z$, b: $+y, 1-x, -z$, c: $1-x, 1-y, +z$, #1:$3/2-x, 1/2+y, 1/2-z$, #2:$1/2+x, 1/2-y, -1/2-z$, #3:$1/2+y, -1/2+x, -1/2+z$, #4:$1/2-y, 1/2-x, 1/2+z$, #5: $-1/2+x, 1/2-y, 1/2-z$, #6:$1/2-x, 1/2+y, -1/2-z$, #9:$1/2-y, 3/2-x, -1/2+z$, #10:$1/2+y, 1/2+x, 1/2+z$.

vacuum caused sublimation of a small amount of a crystalline colorless compound identified as 1,2-ethylene selenate $(CH_2O)_2SeO_2$ (**4**), analogous to the well-known 1,2-ethylene sulfate $(CH_2O)_2SO_2$. This compound is stable only for a very short period of time and could be thus analyzed only by Raman spectroscopy and single-crystal X-ray crystallography. If the supernatant solution was stored at ambient temperature for 5 d instead of being immediately evacuated, the deposition of large colorless crystals of the bicyclic ester $C_2H_2O_8Se_2\cdot(diox)_2$ (**3**) on the walls of the Schlenk flask was observed. Compound **3** was isolated by siphoning the remaining solution into another Schlenk flask, allowing its characterization, but it is highly unstable and decomposes immediately when evacuated. Unfortunately, until now, we were not able to find any reasonable synthesis for **3** and **4**, which would allow the obtainment of these compounds in higher yields, facilitating the study of their reactivity.

The identification of several reaction products and intermediates allowed us to propose the following reaction mechanism for the formation of compounds **1**−**5** and the selenic and diselenic acids (Scheme 1). Thus, in the first step, the adduct **5** is formed, but decomposes upon coordination of a second molecule of SeO_3 to the dioxane molecule into 2 equiv of **4**. In the presence of SeO_3 acting as a base, the cyclic ester **4** is first transformed into the unstable acyclic intermediate $H_2C{=}CHOSe(O)_2OH$, which is similar to that known from the Riley oxidation of acetaldehyde $(H_2C{=}CHOSe(O)OH)$,[1] and is finally converted into glyoxal, "SeO", and water. None of these products are stable in the presence of SeO_3, and thus glyoxal reacts with 2 equiv of SeO_3 to give **3**, whereas "SeO" is oxidized with 1 equiv of SeO_3 and a Se_2O_4 unit is produced. This unit reacts with another equivalent of SeO_3 to form **2**, which forms upon insertion of another SeO_3 unit the cyclic oxide **1**. Water is trapped by 1 or 2 equiv of SeO_3 and forms H_2SeO_4 or the diselenic acid $H_2Se_2O_7$, respectively. Both acids were identified in the reaction mixtures. The deprotonation of **4** in the first step of its transformation to glyoxal is supported by a quite short $CH\cdots O{=}Se$ distance (2.53−2.70 Å) observed in the crystal structure of **4** and also in the dioxane adducts of the oxides **1** (2.42−2.70 Å) and **2** (2.39−2.71 Å).

From these data it is clear that the formation of mixed-valence species **1** and **2** is caused by an insufficient kinetic control due to the high reaction temperature. Thus, CCl_4 was used as an inert solvent in a ratio of 2:1 (dioxane/CCl_4) in an attempt to isolate the simple adduct $SeO_3\cdot diox$ (**5**). The Schlenk flask with SeO_3 was first placed in a liquid nitrogen bath, and CCl_4 was added at such a rate that it completely solidified. Thereafter, the appropriate amount of dioxane was added in the same manner. The reaction mixture was allowed to warm to ambient temperature; once it was partially thawed, it was vigorously stirred. Microcrystalline **5** can be isolated from this reaction mixture by removing all volatiles in vacuum **immediately** after dissolution of all SeO_3. However, compound **5** obtained in this manner is neither stable nor spectroscopically pure. When two-thirds of the volatiles are removed and the resulting solution is stored at ambient temperature for a few days, large, well-defined crystals of spectroscopically pure **2** are formed. The crystals of **2** can be collected in a good yield by a careful decantation of the solution. However, it is not possible to eliminate the solvating dioxane molecules even under vacuum; thus, unsolvated Se_3O_7 should be prepared as reported previously.[13] Few colorless crystals identified as β-$SeCl_4$ were also isolated from the decanted solution after several days, which could be formed only in a reaction of SeO_3 with CCl_4.[14] The possible subproducts of this reaction are phosgene and CO_2. However, all our attempts to confirm their presence in the reaction mixture were futile. Because of this observation, we decided to use in further experiments nitromethane as the diluting solvent. When SeO_3 was first dissolved in nitromethane at low temperature and subsequently dioxane was added at −10 °C, analytically pure $Se_4O_{10}\cdot(diox)_2$ (**1**) could be isolated in a 30% yield after storing the reaction mixture at −30 °C for several days. Formally, compound **1** is a cyclic polymorph (as identified by X-ray diffraction, *vide infra*) of the well-known stable polymeric oxide Se_2O_5 that can be obtained from **1** upon evacuating the dioxane.[15] Therefore, any attempt to recrystallize **1** to obtain X-ray quality crystals has to be done from a diluted nitromethane/dioxane mixture due to the solubility of **1**. In most cases, redox products were observed before formation of sufficiently large crystals of **1**. However, after multiple attempts it was possible to obtain crystals of sufficient quality to determine the crystal structure of **1**. From the previous reactions it was clear that the desired adduct $SeO_3\cdot diox$ (**5**) was not stable when dissolved in organic solvents. Thus, we used liquid sulfur dioxide as a solvent, as it should allow the precipitation of **5** immediately after its formation. When SeO_3 was dissolved in liquid SO_2 and dioxane was added at low temperature, a white microcrystalline solid identified as **5** formed immediately. After cooling the solution to −10 °C, analytically pure **5** was isolated in a nearly quantitative yield, thus suppressing almost all side reactions. Single crystals of **5** were obtained by recrystallization from nitromethane.

During the purification of SeO_3 via sublimation, prismatic single crystals of the unstable form of SeO_3 suitable for single-crystal X-ray analysis were obtained. This unstable form was identified by Paetzold and Amoulong[16] in 1965 using infrared spectroscopy and was assumed to be formed also by a tetrameric $(SeO_3)_4$, albeit with a D_{2d} II conformation. The crystal structure of the stable modification of SeO_3 was determined in 1964 by Mijlhoff[17] and exhibits an S_4 conformation. The assignment of the vibration spectra for both forms was challenged in 1987 by N. J. Brassington.[18] Nonetheless, the spectra used in his work are incorrect and belong to solid SeO_2, which suggests that those conclusions are misleading. Also, our measurements confirm the correct assignment of the spectra in the work of Paetzold and Amoulong for both isomers.

Table 1. Crystallographic Data and Refinement Details for $(SeO_3)_3$ and $(SeO_3)_4$

	$(SeO_3)_3$	$(SeO_3)_4$[a]
chemical formula	O_9Se_3	$O_{12}Se_4$
formula weight	380.88	507.84
space group	$P2_1/c$ (No. 14)	$P\bar{4}2_1c$ (No. 114)
a/Å	7.008(2)	9.527(3)
b/Å	20.213(6)	9.527(3)
c/Å	5.462(2)	5.171(1)
α/deg	90	90
β/deg	109.64(3)	90
γ/deg	90	90
V/Å^3	728.7(4)	469.3(3)
Z	4	2
T/K	153(2)	153(2)
λ/Å	0.710 73	0.710 73
μ/mm^{-1}	15.163	15.694
$\rho_{calc.}$/g·cm^{-3}	3.472	3.569
R_1 ($I > 2\sigma(I)$)[b]	0.0512	0.0298
wR_2 (all data)[c]	0.1443	0.0752

[a]Flack parameter = 0.03(4). [b]$R_1 = \sum||F_0| - |F_c||/\sum|F_0|$. [c]$wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum(F_0^2)^2]^{1/2}$.

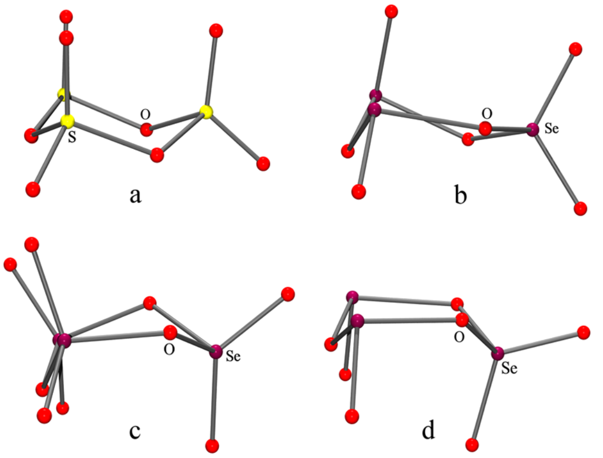


Figure 2. Conformation of the six-membered ring in (a) $(SO_3)_3$, (b) **2**, (c) $(SeO_3)_3$, and (d) $Se_3O_7{\cdot}CH_3NO_2$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(SeO_3)_3$ and $(SeO_3)_4$

	$(SeO_3)_3$[a]	$(SeO_3)_4$[a]
$Se^{VI}{=}O$	1.567(6)−1.582(6)	1.567(6), 1.573(6)
$Se^{VI}{-}O$	1.755(5)−1.794(6)	1.771(6), 1.778(5)
$Se^{VI}{\cdots}O$	3.025(6)−3.325(6)	3.126(6), 3.150(6)
$O{=}Se^{VI}{=}O$	125.4(4)−128.2(4)	128.5(3)
$O{-}Se^{VI}{-}O$	97.3(3)−98.8(2)	98.2(3)
$O{=}Se^{VI}{-}O$	103.4(3)−111.8(3)	101.9(3)−110.4(3)
$Se^{VI}{-}O{-}Se^{VI}$	122.3(3)−124.8(3)	122.4(3)
$O{\cdots}Se^{VI}{\cdots}O$	116.5(3)−126.6(3)	104.8(3)

[a]In case of various values, only the range is given.

Upon heating, the crystals of the unstable modification start to change into thin and, later, into quite thick fibers until they melt at 94 °C. However, the melt immediately solidifies and melts again at 121 °C, which corresponds to the melting point of the stable modification $(SeO_3)_4$. This transformation takes between days (at ambient temperature) to seconds at the melting point or higher temperatures and is irreversible. It was not possible to identify monomeric SeO_3 during this transformation; therefore, the trimeric molecules most probably transform directly into the tetramers. X-ray diffraction studies revealed that the unstable modification is formed by cyclic trimeric $(SeO_3)_3$ molecules and crystallizes in the monoclinic space group $P2_1/c$ with one molecule of the trimer in the asymmetric unit (Figure 1, Table 1). This is a strikingly different constitution than that predicted by Paetzold and Amoulong. The six-membered Se_3O_3 ring has a slightly twisted boat conformation, similar to that in $Se_3O_7{\cdot}CH_3NO_2$,[13] but is less deformed than that in **2** (Figure 2). This can be explained by the equatorial position of both oxo groups bound to the Se^{IV} atoms due to their *cis* orientation in $Se_3O_7{\cdot}CH_3NO_2$, which results in a similar conformation to that in $(SeO_3)_3$, while the *trans* orientation of these oxo groups in **2** causes a larger deformation from the boat conformation as one of the oxo group is in equatorial position while the other is in the nonpreferred axial position. On the other side, the S_3O_3 ring in the trimeric γ-modification of sulfur trioxide has a chair conformation (Figure 2).[19] The presence of the unstable form in the solid sample can be easily determined by the presence of a characteristic absorption band at $\tilde{\nu}$ 405 cm^{-1} in its Raman spectrum. Further confirmation of its presence can be done using the bands for the ν_sSeOSe vibrations at $\tilde{\nu}$ 534, 553, and 593 cm^{-1}, which are found at significantly higher wavenumbers than the corresponding absorption bands for the stable form $(SeO_3)_4$ $\tilde{\nu}$ 508, 529, and 583 cm^{-1}. To be able to precisely describe the differences in bond lengths and angles between the stable tetrameric and unstable trimeric form of SeO_3 or **1**, it was necessary to redeterminate the crystal structure of the stable form,[17] which crystallizes in the tetragonal $P\bar{4}2_1c$ space group with one-half of the molecule in the asymmetric unit. Surprisingly, the values for Se=O and Se−O bond lengths and O=Se=O, O=Se−O, and O−Se−O angles are practically identical for both forms, from which it may be concluded that the ring strain is also similar (Table 2). The main differences between the two forms are the intermolecular interactions. In both forms, two faces of each SeO_4 tetrahedron are capped by an oxygen atom from an oxo group (O=Se) from another molecule. In $(SeO_3)_3$, these Se···O

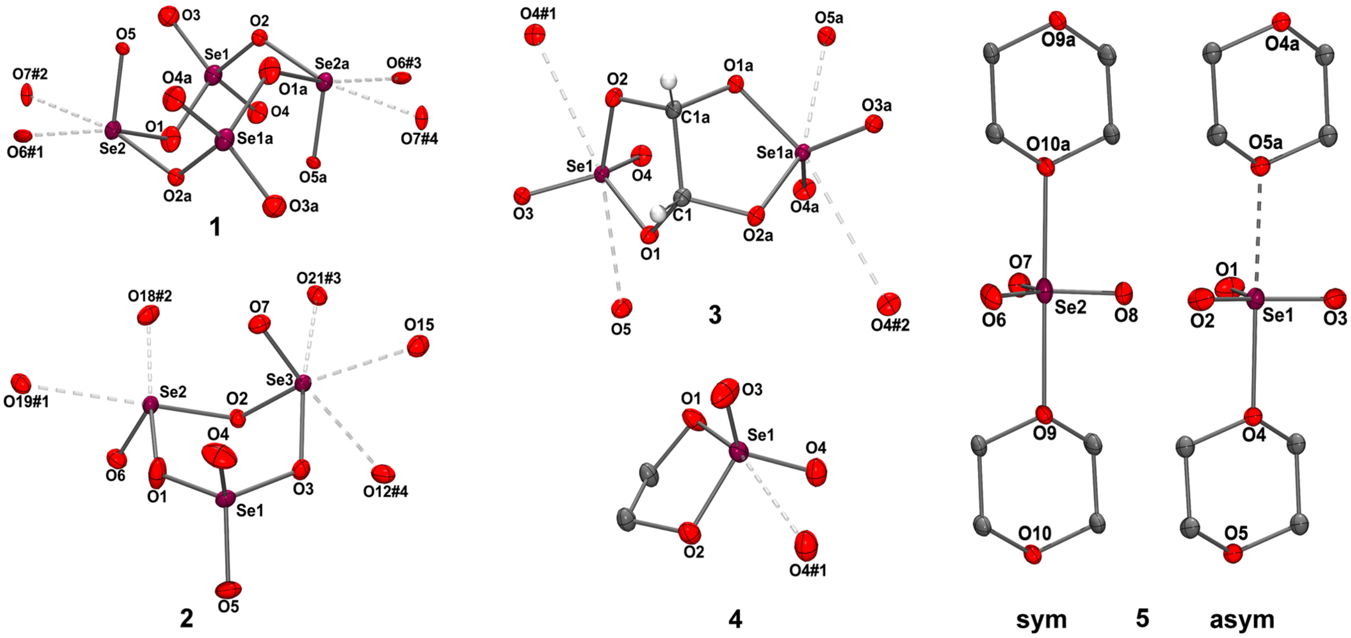


Figure 3. Crystal structures of compounds **1**−**5** with thermal ellipsoids at 50% probability showing close contacts of the selenium atoms to neighboring oxygen atoms. All hydrogen atoms and the second independent molecule of **2** have been eliminated for clarity. Symmetry codes to generate equivalent atoms for **1** #1: +*x*, 1/2 − *y*, 1/2 + *z*, #2: 1 − *x*, 1 − *y*, 1 − *z*, #3: −*x*, 1/2 + *y*, #4: 1/2 − *z* −1 + *x*, +*y*, +*z*; **2** #1: 1/2 + *x*, 1/2 − *y*, −1/2 + *z*, #2: 3/2 − *x*, −1/2 + *y*, 1/2 − *z*, #3: 1 − *x*, 1 − *y*, 1 − *z*, #4: +*x*, −1 + *y*, +*z*; **3** a: 1/2 − *x*, +*y*, 1 − *z*, #2: 1 − *x*, 1 − *y*, 1 − *z*, #2 −1/2 + *x*, 1 − *y*, +*z*; **4** #1: 1 −*x*, 1 −*y*, −*z*; **5 sym** a: 1 + *x*, +*y*, +*z*; **5 asym** a: −1 + *x*, +*y*, +*z*.

contacts show relatively large variation (3.025 to 3.325 Å), while in $(SeO_3)_4$, they are smaller (between 3.126 and 3.150 Å) and in the lower half of the former range. On the other hand, the O···Se···O angle in $(SeO_3)_4$ (104.8°) is smaller than those in $(SeO_3)_3$ (116.5−126.6°). Thus, it can be suggested that these intermolecular contacts with higher symmetry of the molecule are responsible for the higher stability of the tetrameric form.

Compounds **1**−**3** crystallize in the monoclinic space groups $P2_1/c$, $P2_1/n$, and $I2/a$, respectively, with one molecule of Se_4O_{10} and two dioxane molecules (**1**), two molecules of Se_3O_7 each solvated by two dioxane molecules (**2**), and half a molecule of the glyoxal selenate with half a molecule of dioxane in the asymmetric unit (**3**). Compound **4** crystallizes in the orthorhombic *Pbca* space group with one molecule of **4** in the asymmetric unit, whereas compound **5** crystallizes in the triclinic $P\overline{1}$ space group with two independent molecules of SeO_3 each solvated by one dioxane molecule in the asymmetric unit (Figure 3, Table 3). In compounds **1** and **2**, the interactions of the Se^{IV} atoms with oxygen atoms from dioxane (**1** and **2**) and the $Se^{VI}{=}O$ oxo units (only in **2**) result in a tetragonal-pyramidal or octahedral coordination. In both compounds, the dioxane molecules coordinate *trans* to the endocyclic oxygen atoms, whereas the oxo group coordinates to the selenium atoms Se(3) and Se(5) *trans* to the oxo group. It is noteworthy that in both independent molecules of **2** only one of the Se^{IV} atoms is hexacoordinated, most probably due to the steric hindrance caused by the crystal packing. The Se^{IV}···O(diox) contacts are symmetric and shorter in the case of **1** (2.403 and 2.440 Å) than those observed for **2** (molecule 1 = 2.486−2.618 Å, molecule 2 = 2.435−2.652 Å). The variation of length of these contacts between the two crystallographically different molecules of **2** confirms that these contacts are governed by the crystal packing. The $Se^{VI}{=}O\cdots Se^{IV}$ interactions are with 3.065 and 2.820 Å, significantly longer that the interaction of Se^{IV}···O(diox). The absence of Se^{IV} atoms in compounds **3**−**5** allows for the formation of such interactions with the Se^{VI} atoms. As the four directly bounded oxygen atoms adopt tetrahedral geometry around the selenium atoms, these interactions are "capping" one or both faces of this tetrahedron formed by both oxo atoms and one endocyclic oxygen atom. In compound **3**, the distances between the dioxane molecules and the Se^{VI} ion are asymmetrical (2.826 and 3.132 Å), whereas the absence of solvating dioxane in **4** results in only one interaction (3.172 Å). These interactions are similar to those observed in $(SeO_3)_3$ and $(SeO_3)_4$. In compound **5**, the situation is different due to the planarity of the SeO_3 unit, and the coordination of two molecules of dioxane to the SeO_3 monomer results in a trigonal bipyramidal coordination sphere for both independent Se atoms, with the dioxane oxygen atoms in the axial positions. Surprisingly, in case of Se(1), these contacts are with 2.314 Å, symmetrical, but in case of Se(2), one dioxane molecule is coordinated far more strongly than the other (2.189 and 2.460 Å). These values are significantly longer than those observed in the adduct $SeO_3{\cdot}OEt_2$ (1.993 Å) and are roughly comparable to those for $SeO_3{\cdot}(OMe_2)_2$ (2.240 and 2.272 Å).[6]

In compounds **1**−**5**, $(SeO_3)_3$, and $(SeO_3)_4$, all Se═O bond lengths fall into a narrow interval of 1.567−1.603 Å, confirming that they are not affected by the oxidation state of the selenium. However, there is a clear difference between the $Se^{VI}{-}O$ (1.688−1.758 Å) and $Se^{IV}{-}O$ (1.755−1.958 Å) bond lengths. Particularly, the value for the bond between Se(2) and O(1) in the first molecule of **2** is 1.958(2) Å, close to the value for a donor−acceptor bond found in $SeO_3{\cdot}OEt_2$ (1.993 Å), indicating a weak nature of this bond. However, both values are comparable to the sum of covalent radii for selenium and oxygen (1.9 Å). The presence of five-membered rings in compounds **3** and **5** deforms the endocyclic O−Se−O angles to 91.5(1) and 94.4(1)°, respectively. These are slightly smaller than those in $(SeO_3)_3$ and $(SeO_3)_4$ (97.3−98.8°) and much less

Table 3. Crystallographic Data and Refinement Details for Compounds 1−5

	1	2	3	4	5
chemical formula	$C_8H_{16}O_{14}Se_4$	$C_8H_{16}O_{11}Se_3$	$C_6H_{10}O_{10}Se_2$	$C_2H_4O_4Se$	$C_4H_8O_5Se$
formula weight	652.05	525.09	400.06	171.01	215.06
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14, variant)	$I2/a$ (No. 15, variant)	$Pbca$ (No. 61)	$P\bar{1}$ (No. 2)
a/Å	8.380(1)	17.3762(2)	11.9569(4)	8.499(2)	7.3786(3)
b/Å	8.981(1)	10.8301(1)	5.4306(1)	9.246(2)	10.4307(6)
c/Å	12.025(2)	17.5751(2)	17.4707(8)	11.900(2)	10.6527(5)
α/deg	90	90	90	90	118.799(5)
β/deg	96.03(1)	111.016(2)	94.222(5)	90	93.758(4)
γ/deg	90	90	90	90	105.026(4)
V/Å^3	900.0(2)	3087.38(7)	1131.35(7)	935.1(3)	676.11(7)
Z	2	8	4	8	4
T/K	123(2)	123(2)	123(2)	120(2)	123(2)
λ/Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
μ/mm^{-1}	8.222	7.201	6.583	7.927	5.516
$\rho_{calc.}$/g·cm^{-3}	2.406	2.259	2.349	2.429	2.113
R_1 ($I > 2\sigma(I)$)^a	0.0544	0.0179	0.0124	0.0244	0.0218
wR_2 (all data)^b	0.0882	0.0394	0.0327	0.0568	0.0551

${}^aR_1 = \sum||F_0| - |F_c||/\sum|F_0|$. ${}^bwR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum(F_0^2)^2]^{1/2}$.

obtuse than those in **1** and **2** (105.2−106.4°). The absence of one of the oxo groups on the Se^{IV} atom also reduces the endocyclic O−Se^{IV}−O angles in **1** and **2** to 90.6(3)−94.3(1)°. Because of the short Se═O bond lengths, the observed values for the O═Se═O angles in **1**−**5** belong to a narrow interval of 117.1(1)−121.7(1)°, but they are smaller than those for $(SeO_3)_3$ and $(SeO_3)_4$ (125.4−128.5°). Table 4 summarizes selected bond lengths and angles for compounds **1**−**5**.

The Raman spectra of the mixed-valence selenium oxides **1** and **2**, and that of compound **3**, are complicated due to the presence of solvating dioxane molecules. A relatively small number of Raman lines present in the spectra are caused by the symmetry of the dioxane (C_{2h}), which is conserved also in the crystal structure of the solvates **1**−**3**. The comparison of the individual vibrations suggests that, in the case of compounds **1**−**3**, the values for the solvating dioxane molecules differ only slightly from the values for a free dioxane molecule.[20]

The higher symmetry of the molecule of Se_4O_{10} in **1** (D_{2h}) compared to a lower symmetry of Se_3O_7 in **2** (ideally C_2, in reality rather C_1 due to different Se^{IV}−O bond lengths) results in a simpler spectrum for **1**, where one can observe the vibration bands at $\tilde{\nu}$ 926 and 994 cm^{-1}, which can be unequivocally assigned to the valence vibrations $\nu_{s+as}Se^{VI}O_2$ in the cycle of **1**. The wavenumbers of these bands in Se_3O_7 in **2** ($\tilde{\nu}$ 921 and 987 cm^{-1}) are practically identical. Also in the case of the vibrations $\nu_{s+as}Se^{IV}O$ in **1** ($\tilde{\nu}$ 826 cm^{-1}) and **2** ($\tilde{\nu}$ 819 and 824 cm^{-1}) the values show only slight differences. In the spectrum of **2** it is further possible to identify bands belonging to the ν_{as}SeOSe vibrations at $\tilde{\nu}$ 615 and 568 cm^{-1}. The doubling of these bands in **2** is caused by the unequivalency of the Se^{IV}-containing groups. Also, the symmetry and conformation of Se_3O_7 in **2** is highly different than that observed for Se_3O_7 in $Se_3O_7 \cdot CH_3NO_2$.[13] The Raman spectra of the cyclic esters **3** and **4** exhibit strong bands at $\tilde{\nu}$ 943 (**3**) and 934 (**4**) cm^{-1}, respectively, belonging to the $Se^{VI}O_2$ moieties. This is in agreement with the Raman spectra of salts of diselenic acid, where one can observe the $\nu_{s+as}SeO_2$ vibrations in the interval of $\tilde{\nu}$ 940−960 cm^{-1}.[21] The lines at $\tilde{\nu}$ 638 and 696 cm^{-1} in the spectrum of **3** belong to the group νSeO(C), as does the most intense line in the spectrum of **4** at $\tilde{\nu}$ 670 cm^{-1}.[22] The organic parts in **3** (O_2CH−CHO_2) and **4** (OCH_2−CH_2O) generate bands between $\tilde{\nu}$ 2856 and 3020 cm^{-1} (**3**) and $\tilde{\nu}$ 2890 and 3045 cm^{-1} (**4**) for the valence vibrations of C−H bonds. The deformation vibrations of these organic skeletons in **3** and **4** can be found at $\tilde{\nu}$ 1399 and 1444 cm^{-1} (**3**) and at $\tilde{\nu}$ 1363, 1452, and 1461 cm^{-1} (**4**), respectively. Similarly, it was possible to identify the bands for the valence C−O vibrations ($\tilde{\nu}$ 1217, 1283, and 1291 cm^{-1} in **3** and $\tilde{\nu}$ 1211 and 1228 cm^{-1} in **4**). The highest symmetry of the molecule of the adduct **5** in the crystal can be only C_s, and thus the Raman spectrum of **5** can contain all 48 normal vibrations. However, due to the presence of a very intense valence vibration of the ν_sSeO_3 group at $\tilde{\nu}$ 876 cm^{-1}, the intensities of all other vibrations are rather an order of magnitude smaller. Such a strong band was observed in the range of $\tilde{\nu}$ 870−882 cm^{-1} in all confirmed adducts of SeO_3 with O-donors and can be thus considered as a spectroscopic proof of the formation of such adducts.[6] Because of the low intensity of the remaining vibrations in the spectra of **5**, the identification of the breathing vibrations of the dioxane ring is quite difficult, and thus it is not possible to elucidate the changes in the electronic structure of the dioxane molecule caused by its coordination to the SeO_3 unit. However, it is possible to observe the band belonging to the ν_sCOC vibration of dioxane in **5** at $\tilde{\nu}$ 803 cm^{-1}, which is at a significantly lower wavenumber that the one observed for a free dioxane ($\tilde{\nu}$ 835 cm^{-1}). The deformation vibrations ω and τ of the CH_2 groups can be found at $\tilde{\nu}$ 1211 and 1305 cm^{-1}, respectively. The bonding situation in the polymeric structure of **5** is similar to that in the monomeric $SeO_3 \cdot (OMe_2)_2$, which has also the selenium atom in a trigonal bypiramidal environment. However, the Se···O(diox) distances in $SeO_3 \cdot (OMe_2)_2$ are symmetrical (2.24 and 2.27 Å), and the ν_sSeO_3 vibration can be found at $\tilde{\nu}$ 881 cm^{-1}, whereas in the asymmetric molecule of **5**, the Se···O(diox) distances are 2.19 and 2.46 Å; when averaged, these bonds are identical to those in the symmetric molecule of **5** (2.31 Å) and can be considered weaker than those in $SeO_3 \cdot (OMe_2)_2$, which is in agreement with the observation of a ν_sSeO_3 vibration in **5** at a lower wavenumber of $\tilde{\nu}$ 876 cm^{-1}.[6] Table 5 summarizes the most important Raman bands for compounds **1**−**5** (full Raman spectra for these compounds can be found in the Supporting Information).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1–5

	1	2		3	4	5	
		molecule 1	molecule 2			asym	sym
$Se^{VI}{=}O$	1.588(6), 1.600(6)	1.588(2), 1.590(1)	1.586(2), 1.590(2)	1.586(1), 1.592(1)	1.584(2), 1.589(2)	1.591(2)−1.596(2)	1.589(2)−1.597(2)
$Se^{IV}{=}O$	1.582(6)	1.585(1), 1.603(1)	1.587(1), 1.593(1)				
$Se^{VI}{-}O$	1.705(7), 1.735(6)	1.688(2), 1.717(1)	1.702(1), 1.706(1)	1.758(1), 1.772(1)	1.730(2), 1.732(2)		
$Se^{IV}{-}O$	1.888(6), 1.921(6)	1.796(1)−1.958(2)	1.799(1)−1.924(1)				
C−O(Se)				1.402(2), 1.439(2)	1.465(3), 1.467(3)		
Se···O(Se)		2.820(2)	3.065(2)	3.132(1)	3.172(2)		
Se···O(diox)	2.403(6), 2.440(6)	2.436(2)−2.652(1)	2.486(1)−2.618(1)	2.826(1)		2.189(2), 2.461(1)	2.314(2), 2.314(2)
$O{=}Se^{VI}{=}O$	119.7(3)	117.1(1)	117.6(1)	121.7(1)	119.0(1)	118.9(1)−121.3(1)	118.8(1)−120.9(1)
$O{-}Se^{VI}{-}O$	105.2(3)	106.4(1)	105.2(1)	91.5(1)	94.4(1)		
$O{=}Se^{VI}{-}O$	104.2(3)−111.9(3)	106.0(1)−110.0(1)	105.8(1)−110.5(1)	107.9(1)−112.4(1)	107.6(1)−112.7(1)		
$Se^{VI}{-}O{-}Se^{IV}$	125.6(4), 127.2(3)	122.5(1), 133.4(1)	124.3(1), 130.4(1)				
$Se^{IV}{-}O{-}Se^{IV}$		116.1(1)	121.3(1)				
$O{-}Se^{IV}{-}O$	90.6(3)	92.4(1), 92.6(1)	92.9(1), 94.3(1)				
$O{=}Se^{IV}{-}O$	101.7(3), 102.9(3)	97.7(1)−101.8(1)	99.2(1)−103.6(1)				
$O{=}Se^{IV}\cdots O$(diox)	87.8(3), 87.8(3)	83.9(1)−92.1(6)	88.1(1)−89.5(1)	75.0(1)−84.8(1)		86.9(1)−94.0(1)	87.8(1)−91.6(1)
$O{-}Se^{IV}\cdots O$(diox)	90.9(3), 91.9(3)	82.6(1)−86.4(1)	82.5(1)−86.6(1)	69.5(1)			
	168.6(3), 169.3(3)	165.9(1)−176.3(1)	166.8(1)−174.3(1)	159.8(1)			
$O{=}Se^{IV}\cdots O$(Se)		175.6(1)	167.7(1)	73.4(1), 78.4(1)[a]	74.4(1), 76.6(1)[a]		
$O{-}Se^{IV}\cdots O$(Se)		81.4(1), 81.5(1)	76.0(1), 90.4(1)	70.5(1), 161.9(1)[a]	74.3(1), 168.6(1)[a]		
$O\cdots Se^{IV}\cdots O$	84.6(2)	84.8(1)−96.2(1)	79.6(1)−96.6(1)	128.2(1)[a]		177.5(1)[a]	177.8(1)[a]

[a] Angles on Se^{VI} instead of Se^{IV}.

Table 5. Selected Raman Shifts for Compounds 1−5

	1	2	$3^{a,b}$	4^{a}	5
$\nu_s SeO_3$					876
$\nu_{s+as} Se^{VI}O_2$	924, 926	921, 987	943	934	
$\nu_{s+as} Se^{IV}O$	826	819, 824			
$\nu_{s+as} SeOSe$	594, 716	568, 615			
$\nu SeO(C)$			638, 696	670	
$\nu CH_{val.}$			2856−3020	2890−3045	
$\nu CH_{def.}$			1399, 1444	1363, 1452, 1461	
$\nu CO_{val.}$			1217, 1283, 1291	1211, 1228	

[a] Vibrations only for the organic residues incorporated in the selenium-containing cycles. [b] $\nu CH_{val.}$, $\nu CH_{def.}$.

■ CONCLUSION

The kinetic control over the reaction of selenium trioxide with dioxane allowed isolation of the first cyclic esters of selenic acid, two different modifications of mixed-valence selenium oxides Se_4O_{10} and *trans*-Se_3O_7, and the monomeric adduct $SeO_3 \cdot diox$. Furthermore, it was possible to determine the structure of the unstable modification of selenium trioxide $(SeO_3)_3$. These results enrich substantively the chemistry of Se^{VI}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional crystallographic details and full Raman spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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