Z. anorg. allg. Chem. 622 (1996) 1617—1622

Zeitschrift für anorganische
und allgemeine Chemie

Synthesis and Structure of Cyclic Selenium Oxide $Se^{VI}Se_2^{IV}O_7$

J. Toužín*, P. Kilián and Z. Žák

Brno/Czech Republic, Masaryk University, Department of Inorganic Chemistry

Received December 28th, 1995.

Abstract. Nitromethane is the only presently known organic solvent for highly reactive selenium trioxide $(SeO_3)_4$. The stability of the solutions is limited and the beginning of the reaction between both components depends significantly on concentration and temperature. The nitromethane solvate of cyclic triselenium heptoxide $Se_3O_7 \cdot CH_3NO_2$ is the major solid product at the temperature 20 – 30 °C and concentration range 3 – 20% SeO_3. Crystal and molecular structure of this compound was determined by X-ray structure analysis and vibrational spectroscopy. The solvating molecule CH_3NO_2 is removable from $Se_3O_7 \cdot CH_3NO_2$ *in vacuo*. If reaction temperature does not exceed 10 °C, selenium pentoxide $(Se_2O_5)_n$ is formed instead of $Se_3O_7 \cdot CH_3NO_2$. Dinitrosyl triselenate $(NO)_2Se_3O_{10}$, nitrosyl hydrogendiselenate $NOHSe_2O_7$, nitrosyl hydrogenselenate $NOHSeO_4$, nitrosyl hydrogenselenatoselenite $NOHSe_2O_6$ and selenium dioxide $(SeO_2)_n$ were further identified in the solid reaction products. The selenic and/or oligoselenic acids remains in the nitromethane solution. CO_2 and N_2O_3 were found as gaseous products.

Synthese und Struktur des zyklischen Selenoxides $Se^{VI}Se_2^{IV}O_7$

Inhaltsübersicht. Nitromethan gilt als das einzige organische Lösungsmittel für Selentrioxid. Die Stabilität der Lösungen ist beschränkt und in Abhängigkeit von Temperatur und Konzentration an $(SeO_3)_4$ tritt eine Reaktion zwischen beiden Komponenten ein. Im Konzentrationsbereich 3 – 20% SeO_3 und bei 20 – 30 °C wird das Monosolvat des Triselenheptoxides $Se_3O_7 \cdot CH_3NO_2$ als Hauptprodukt gebildet. Dessen Kristall- und Molekülstruktur wurde durch Röntgen-Kristallstrukturanalyse und Schwingungsspektren bestimmt. Im Vakuum bei 20 °C ist das Solvatmolekül CH_3NO_2 leicht abspaltbar. Haben die Selentrioxidlösungen eine Temperatur unterhalb 10 °C, entsteht nicht das Triselenheptoxid, sondern das Diselenpentoxid $(Se_2O_5)_n$. Als weitere feste Reaktionprodukte wurden Dinitrosyltriselenat $(NO)_2Se_3O_{10}$, Nitrosylhydrogendiselenat $NOHSe_2O_7$, Nitrosylhydrogenselenat $NOHSeO_4$, Nitrosylhydrogenselenatoselenit $NOHSe_2O_6$ und Selendioxid $(SeO_2)_n$ identifiziert. In der Mutterlösung bleibt die Selensäure (oder Oligoselensäuren) zurück. CO_2 und N_2O_3 wurden als gasförmige Reaktionsprodukte festgestellt.

Keywords: Seleniumoxide; nitrosylhydrogenoligoselenate; nitrosylhydrogenselenatoselenite; preparation; crystal structure; molecular structure; vibrational spectra

1 Introduction

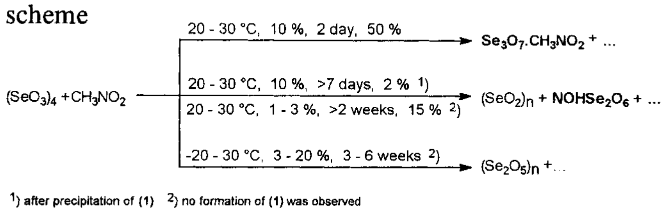
Nitromethane is used for solving both selenium trioxide and sulphur trioxide. The stability of both solutions is limited by time and concentration. The exothermic reaction of sulphur trioxide with nitromethane gives a mixture of O-hydroxylaminemonosulphuric acid and amidosulphuric acid [1]. When concentration of solution is raised over 35%, the reaction has an explosive character. It is assumed that monomeric SO_3 enters into the reaction and hydroxylamine as an intermediate is formed in analogy with reactions of nitroalkanes with mineral acids [2].

Selenium trioxide dissolves in CH_3NO_2 to colourless solution and there is relative long time interval between its preparation and formation of first reaction products. During this interval $(SeO_3)_4$ can be obtained back or it is possible to realize many of its reactions with other compounds [3 – 5]. Since it has been proved that selenium trioxide exists in its solutions only as tetrameric molecules [6], we assumed that not only reaction course but also products could be different from the reaction of SO_3 with nitromethane. As reaction products there were identified, isolated and structurally characterized triselenium heptoxide nitromethane solvate $Se_3O_7 \cdot CH_3NO_2$ (**1**) and dinitrosyl triselenate $(NO)_2Se_3O_{10}$ (**2**). The formation of nitrosyl hydrogenselenate $NOHSeO_4$, nitrosyl hydrogendiselenate $NOHSe_2O_7$, nitrosyl hydrogenselenatoselenite $NOHSe_2O_6$, selenium dioxide $(SeO_2)_n$, selenic acid H_2SeO_4 and/or oligoselenic acids were also found. Therefore several simultaneous and consecutive reactions occur in the system

$(SeO_3)_4/CH_3NO_2$ that give a much wider pallete of products than the system SO_3/CH_3NO_2. The influence of reaction conditions to a relative appearance of mentioned products were semiquantitatively studied in the temperature interval −20 – +30 °C and concentration 1 – 20%.

2 Results and Discussion

The major solid products of the studied reaction as well as reaction conditions (temperature, concentration, start of precipitation and yield related to the total amount of selenium given to the reaction) are evident from the scheme



Besides the major solid products in all cases the small amounts of the $NOHSeO_4$, $NOHSe_2O_7$ and (2) are coprecipitated. In the solution remain selenic acid, CO_2 and N_2O_3.

Crystals of (2) were chosen from solid products of the reaction according to their different crystal habitus and their identity was determined by X-ray structure analysis. Poor quality of $NOHSe_2O_7$ crystals used for the X-ray data collection resulted in a low quality structure and so no data are presented in this paper. However, there can be no doubt about the identity of the compound. Raman spectra of all nitrosyl salts were consistent with IR spectra published earlier [7].

The presence of H_2SeO_4 in the mother solution after isolation of (1) was confirmed by the ^1H NMR spectrum (broad singlet at δ 10.86 ppm) and by the Raman spectrum of the sample obtained by evaporization of CH_3NO_2 from reaction mixture (3 medium intensive bands at 986, 886 and 754 cm^{-1} belonging to ν_{as} SeO_2, ν_s SeO_2 and ν_{s+as} SeOH, respectively [8]). To prove the formation of CO_2 we carried out the reaction of $(SeO_3)_4$ with nitromethane under nitrogen atmosphere and we absorbed forming CO_2 in alkali solution of $BaCl_2$. Colourless precipitate of $BaCO_3$ was identified by IR spectroscopy.

$(NO)HSe_2O_6$ precipitates in a microcrystalline form on the side of the reaction vessel, always together with $(SeO_2)_n$. Amount of $(SeO_2)_n$ in the mixture continually rises with lengthening of reaction time. Suitable solvent for this product was not found and therefore the only method used for its identification was vibrational spectroscopy.

We were not able affect the quality of crystals of **(1)** to be fully suitable for X-ray analysis by changing reaction conditions. The crystals are very thin soft plates and they mostly form aggregates. The effort to find a suitable solvent for preparation of single crystals was not successful and so the crystal for X-ray analysis had to be taken directly from the reaction mixture after several months standing for recrystallization of **(1)** in mother liquid at −20 °C.

Nitromethane is bound very weakly in the solvate and in the stream of dry air it is partialy released and can be removed quantitatively at room temperature and pressure of ca 100 Pa during 10 hours. The desolvation can be very well checked by means of IR spectroscopy through changing the intensities of bands at 1565 and 1103 cm^{-1} belonging to the vibrations ν_{as} NO_2 and ρ CH_3 in CH_3NO_2. Using of Raman spectroscopy is also possible (see Figure 3). Nitrosyl salts of oligoselenic acids can be removed from the crude **(1)** via extraction with liquid SO_2. At room temperature pure Se_3O_7 is stable during several weeks and both it and its solvate are highly hygroscopic. It cannot be sublimed *in vacuo,* at normal pressure it starts to be rapidly thermally decomposed into $(SeO_2)_n$ and O_2 at 215 °C.

X-ray Structure Analysis

$Se_3O_7 \cdot CH_3NO_2$ (1)

A perspective view of the molecule together with its intermolecular contacts is in the Figure 1. The molecule possesses a tub configuration with Se(1) and O(5) atoms being 0.69 and 0.61 Å above the mean plane defined by O(3), O(7), Se(2), and Se(3) respectively. The interatomic distances can be best compared with those in Se_2O_5 [9] which also contains selenium atoms in two valency states. There is an apparent similarity in the bond lengths and the character of intermolecular contacts between these two compounds and all corresponding Se—O distances are equal within 3σ limits: Se^{VI}—O 1.59 – 1.68(3) Å in **(1)**, 1.566 – 1.732(1) Å in $(Se_2O_5)_n$;

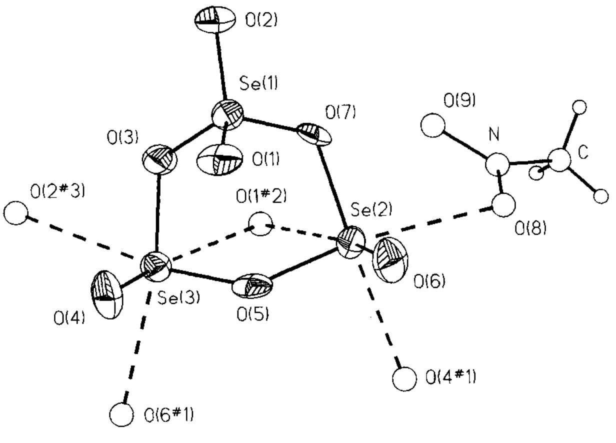


Fig. 1 A perspective view of $Se_3O_7 \cdot CH_3NO_2$ with its intermolecular contacts (thermal ellipsoids drawn with 50% probability)

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[1] after precipitation of (1)

[2] no formation of (1) was observed

$Se^{IV}—O_{bridge} \cdots Se^{VI}$ 1.85 and 1.97(2) Å in (**1**), 1.875 and 1.918(1) Å in $(Se_2O_5)_n$; $Se^{IV}—O$ 1.62 and 1.67(3) Å in (**1**), 1.599(1) Å in $(Se_2O_5)_n$. The distances $Se^{IV}—O_{bridge} \cdots Se^{IV}$, 1.76 and 1.85(2) Å, which have no match in $(Se_2O_5)_n$, compare well with those in $(SeO_2)_n$ (1.74 and 1.80(3) Å [10]). The environment around the $Se^{VI}(1)$ is tetrahedral without any intermolecular contacts but a pyramidal coordination of the $Se^{IV}(2)$ and $Se^{IV}(3)$ atoms is completed to octahedral by neighbouring molecules and that of the solvent (Figure 1) at the distances substantially less than the sum of the van der Waal's radii (Se 2.00 Å, O 1.40 Å [11]). The same feature can be found in the structure of $(Se_2O_5)_n$, where intermolecular Se—O contacts are 2.602(1), 2.605(2), and 2.988(2) Å. The bond lengths and interatomic angles are listed in the Table 3.

$(NO)_2Se_3O_{10}$ (2)

The Figure 2 depicts a $Se_3O_{10}^{2-}$ anion with its intermolecular contacts. NO^+ cations do not take part in any intermolecular interactions. The anions are located on crystallographic two-fold axes and bound into a three-dimensional network via additional Se—O contacts. On the contrary to the structure of (**1**) these bonds are significantly weaker, their lengths are almost on the limits of the van der Waal's radii (*vide infra*). There is also a difference in the shape of the whole coordination polyhedra which is a "capped trigonal bipyramide" in this case rather than an octahedron. It is apparent that the free electron pair of the Se^{IV} in (**1**) has to participate in the formation of intermolecular bonds which results in their shortness.

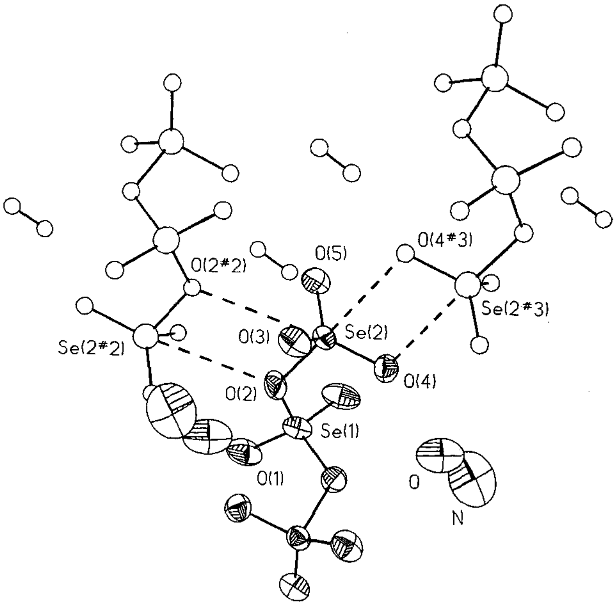

Fig. 2 A perspective view of anions $Se_3O_{10}^{2-}$ with its intermolecular contacts (thermal ellipsoids drawn with 50% probability)

Vibrational Spectra

Raman spectra of both $Se_3O_7 \cdot CH_3NO_2$ and Se_3O_7 together with Raman spectra of the other known Se^{IV} and Se^{VI} oxides are shown in Figure 3. In spite of observed lability of the solvate the contribution of one O atom of the NO_2-group to the coordination on the Se^{IV} atom is connected with a significant change of both positions and intensities of the bands belonging to the solvate molecule vibrations in the region 500 – 1000 cm^{-1} (the bands at 483, 609 and 658 cm^{-1} in the spectrum of CH_3NO_2, the bands at 569, 657 and 712 cm^{-1} in the spectrum of $Se_3O_7 \cdot CH_3NO_2$).

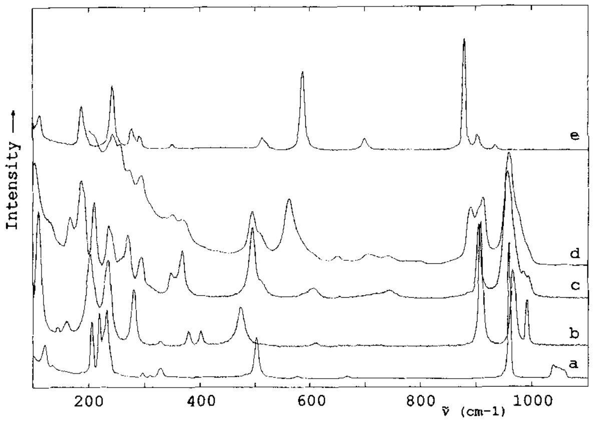

Fig. 3 Raman spectra of solid selenium oxides: a) $(SeO_3)_4$ (S_4-modification), b) $(Se_2O_5)_n$, c) Se_3O_7, d) $Se_3O_7 \cdot CH_3NO_2$ (crystal used for X-ray analysis), e) $(SeO_2)_n$

As for 24 normal vibrations of the Se_3O_7 molecule (symmetry group C_1) four of them belong to the stretching vibrations of the Se=O bonds, six of them belong to the stretching vibrations of Se—O—Se bonds in the cycle and the remaining 14 belong to the deformation vibrations of the cycle and $Se^{VI}O_2$ group. The Raman spectrum of Se_3O_7 can be divided into three non overlapping regions (1000 – 900, 750 – 500 and < 400 cm^{-1}, resp.), in which the above-mentioned vibrations appear. In the first region there presumably appears also an overtone of the intensive band at 502 cm^{-1} besides the four expected normal vibrations. From the six stretching vibrations of the cycle five are detectable in the Raman spectrum. For 14 expected deformation vibrations there can be observed eight well-distinguished bands in the region 100 – 400 cm^{-1}.

The vibrational spectra of the mixture of $NOHSe_2O_6$ and $(SeO_2)_n$ shown in Figure 4 can be interpreted according to the presumed structure of the $[(OH)O_2Se^{VI}O\,Se^{IV}O_2]^-$ anion from the known facts about the vibrational spectra of diselenites (ν_{s+as} SeO_2 815 – 870 cm^{-1}, ν_{as}SeOSe 560 – 580 cm^{-1}, ν_sSeOSe 490 – 515 cm^{-1}) [12, 13], diselenates ($\nu_{s+as}SeO_2$ 940 – 960 cm^{-1}, $\nu_s SeO_3$ 895 cm^{-1}, ν_{as}SeOSe 670 – 700 cm^{-1}, ν_sSeOSe 550 cm^{-1} [14], hydrogenselenates (ν $Se^{VI}O(H)$ 680 – 730 cm^{-1}) [15] and hydrogenselenites (ν $Se^{IV}—O(H)$ 610 – 630 cm^{-1})

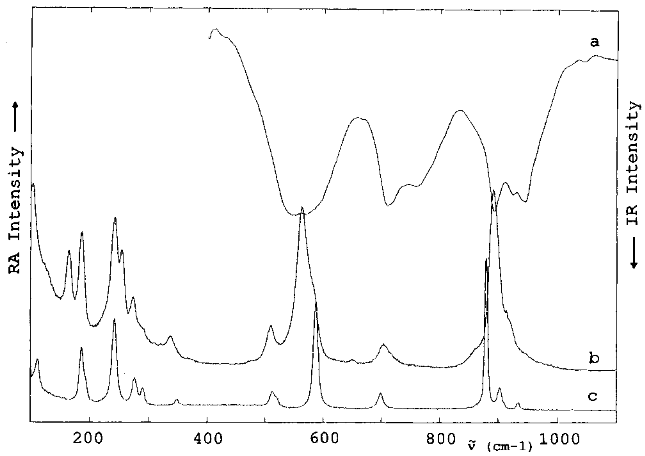

Fig. 4 IR (a) and Raman (b) spectra of a mixture of $NOHSe_2O_6$ and $(SeO_2)_n$, Raman spectrum $(SeO_2)_n$ (c)

Table 1 Crystal data and structure refinement

	1	**2**
Formula	$CH_3NO_9Se_3$	$N_2O_{12}Se_3$
Formula weight	409.92	456.90
Temperature [°C]	298(2)	298(2)
λ [Å]	0.71069	0.71069
System	Monoclinic	Monoclinic
Space group	$P2_1$	C2/c
a [Å]	8.677(3)	14.264(5)
b [Å]	5.096(5)	6.796(2)
c [Å]	10.620(5)	11.417(5)
α [°]	90	90
β [°]	105.68(4)	115.74(4)
γ [°]	90	90
Volume [Å]	452.1(5)	996.9(6)
Z	2	4
F(000)	380	848
D [Mg/m^3]	3.011	3.044
μ [mm^{-1}]	12.234	11.138
Crystal size [mm]	1.00×0.25×0.10	0.80×0.40×0.30
ν range [°]	2.44–25.08	3.17–25.05
Index ranges	$-9 \le h \le 10$ $-2 \le k \le 6$ $-12 \le l \le 6$	$-15 \le h \le 15$ $-8 \le k \le 0$ $-12 \le l \le 0$
All reflections	997	919
Independent	929	868
R(int)	0.1006	0.0670
Refinement	Full matrix least-squares on F	
Weight	$w = 1/[\sigma^2(F_o^2) + aP^2 + bP]$	
	where $P = 0.333[\max \text{ of } (0 \text{ or } F_o^2)] + 0.667 F_c^2$	
Data/parameters	927/128	868/79
S on F^2	1.138	1.055
R-indices [I > 2s(I)]	R1 [a]) = 0.0808 wR2 [b]) = 0.2368	R1 = 0.0410 wR2 = 0.1084
R-indices (all data)	R1 = 0.1023 wR2 = 0.2764	R1 = 0.0486 wR2 = 0.1125
Flack's parameter	0.26(13)	
$\Delta\rho_{max}/\Delta\rho_{min}$	2.256, −1.901	0.928, −0.971

[a]) $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

[b]) $wR2 = [\Sigma w(F_o^2 - F_c^2)/\Sigma w F_o^4]^{1/2}$

[13]. From the position of the band ν Se—O(H) (759 cm^{-1} in the IR spectrum) it can be assumed that the —OH group is located at the Se^{VI} atom. The stretching vibration ν NO of nitrosyl cations appear at 2289 cm^{-1}. The amount of $(SeO_2)_n$ in the sample can be estimated from the intensities of its bands at 582 and 885 cm^{-1}.

3 Experimental

Selenium trioxide $(SeO_3)_4$ was prepared by the dehydration of H_2SeO_4 by P_4O_{10} [16, 17] and resublimed *in vacuo*. Nitromethane was dried with CaH_2, distilled over molecular sieves 4 A and redistilled before use. Liquid sulphur dioxide was dried by P_4O_{10} and distilled. All operations were performed in Schlenk tubes under dry air.

Elemental analyses of Se^{IV} and Se^{VI} were performed volumetrically using iodometric method [18]. ^1H NMR spectra were recorded on a TESLA BS 80 spectrometer and are referred to TMS. IR spectra were obtained in nujol mulls in cells equiped with AgCl windows using a Perkin-Elmer 783 spectrometer. Raman spectra were recorded on a Spex Ramalog 3 spectrometer. The samples were measured in sealed glass capillary tubes, the spectra were excited by the 488 nm line of a Spectra Physics Model 165-03 argon laser (100 mW). Emmision lines of the Ar^+ plasma were employed for the spectral calibration.

The crystal for X-ray Structure Analysis were separated according to their habitus in a special cuvette under a stream of

Table 2 Atomic coordinates (×10) and equivalent isotropic displacement parameters (A×10) for (**1**) and (**2**). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

$Se_3O_7 \cdot CH_3NO_2$ (**1**)				
	x	y	z	U_{eq}
Se(1)	920(3)	3359(8)	8429(3)	29(1)
Se(2)	3668(3)	−86(8)	7844(3)	29(1)
Se(3)	3004(3)	−5(8)	10757(3)	29(1)
O(1)	2135(28)	5793(49)	8935(27)	41(7)
O(2)	−926(26)	3943(66)	7771(25)	45(8)
O(3)	1118(25)	1461(66)	9758(23)	39(6)
O(6)	4651(35)	2466(70)	7454(28)	54(8)
O(4)	3647(35)	2479(62)	11700(26)	48(7)
O(5)	4071(24)	691(44)	9605(23)	31(6)
O(7)	1550(26)	1592(73)	7412(22)	46(8)
N	2450(49)	−3721(75)	5121(39)	54(10)
C	2381(64)	−6005(123)	4210(42)	73(19)
O(8)	3550(53)	−2019(229)	5397(37)	164(40)
O(9)	1303(41)	−3559(103)	5664(32)	78(12)
$(NO)_2Se_3O_{10}$ (**2**)				
	x	y	z	U_{eq}
Se(1)	0	−1804(2)	2500	40(1)
Se(2)	−1269(1)	1239(1)	343(1)	33(1)
O(1)	1069(4)	−2943(9)	2922(5)	61(2)
O(2)	−84(4)	−194(9)	1294(5)	52(1)
O(3)	−705(4)	3173(8)	189(5)	49(1)
O(4)	−1827(4)	1387(7)	1293(5)	45(1)
O(5)	−1841(4)	−84(8)	−913(5)	44(1)
O	−1537(8)	3913(11)	3202(8)	78(2)
N	−1765(11)	3705(15)	3885(14)	111(4)

Table 3 Bond lengths [Å] and angles [°] for (**1**)

Se(1)—O(2)	1.59(2)	Se(3)—O(4)	1.62(3)
Se(1)—O(7)	1.61(3)	Se(3)—O(5)	1.76(2)
Se(1)—O(1)	1.62(3)	Se(3)—O(3)	1.85(2)
Se(1)—O(3)	1.68(3)	N—O(8)	1.26(9)
Se(2)—O(6)	1.67(3)	N—O(9)	1.28(5)
Se(2)—O(5)	1.85(2)	N—C	1.50(6)
Se(2)—O(7)	1.97(2)		
Intermolecular contacts:			
Se(2)—O(4)#1	2.57(3)	Se(3)—O(6)#1	2.71(3)
Se(2)—O(8)	2.75(6)	Se(3)—O(2)#3	2.74(2)
Se(2)—O(1)#2	2.89(3)	Se(3)-O(1)#2	2.85(2)
O(2)—Se(1)—O(7)	107.1(13)	O(4)—Se(3)—O(5)	96.6(12)
O(2)—Se(1)—O(1)	119.3(14)	O(4)—Se(3)—O(3)	98(2)
O(7)—Se(1)—O(1)	110(2)	O(5)—Se(3)—O(3)	94.0(9)
O(2)—Se(1)—O(3)	109.8(13)	Se(1)—O(3)—Se(3)	126.0(12)
O(7)—Se(1)—O(3)	105(2)	Se(3)—O(5)—Se(2)	132.0(13)
O(1)—Se(1)—O(3)	104.6(14)	Se(1)—O(7)—Se(2)	123.5(13)
O(6)—Se(2)—O(5)	96.6(13)	O(8)—N—O(9)	119(5)
O(6)—Se(2)—O(7)	96.4(14)	O(8)—N—C	125(5)
O(5)—Se(2)—O(7)	93.0(9)	O(9)—N—C	116(4)
Intermolecular angles:			
O(6)—Se(2)—O(4)#1	85.7(12)	O(4)—Se(3)—O(6)#1	82.5(13)
O(5)—Se(2)—O(4)#1	89.9(9)	O(5)—Se(3)—O(6)#1	98.5(9)
O(7)—Se(2)—O(4)#1	176.2(12)	O(3)—Se(3)—O(6)#1	167.3(9)
O(6)—Se(2)—O(8)	86(2)	O(4)—Se(3)—O(2)#3	88.3(11)
O(5)—Se(2)—O(8)	168(2)	O(5)—Se(3)—O(2)#3	171.1(9)
O(7)—Se(2)—O(8)	98(2)	O(3)—Se(3)—O(2)#3	77.8(9)
O(4)#1—Se(2)—O(8)	79(2)	O(6)#1—Se(3)—O(2)#3	89.5(8)
O(6)—Se(2)—O(1)#2	171.1(12)	O(4)—Se(3)—O(1)#2	173.3(11)
O(5)—Se(2)—O(1)#2	74.5(9)	O(5)—Se(3)—O(1)#2	76.8(9)
O(7)—Se(2)—O(1)#2	84.7(11)	O(3)—Se(3)—O(1)#2	83.3(11)
O(4)#1—Se(2)—O(1)#2	93.8(8)	O(6)#1—Se(3)—O(1)#2	97.5(8)
O(8)—Se(2)—O(1)#2	102(2)	O(2)#3—Se(3)—O(1)#2	98.4(8)
N—O(8)—Se(2)	107(3)		

Symmetry transformations used to generate equivalent atoms:
#1 −x + 1, y − 1/2, −z + 2
#2 x, y − 1, z
#3 −x, y − 1/2, −z + 2

Table 4 Bond lengths [Å] and angles [°] for (**2**)

Se(1)—O(1)	1.587(5)	Se(2)—O(4)	1.603(5)
Se(1)—O(2)	1.722(5)	Se(2)—O(2)	1.841(4)
Se(2)—O(5)	1.586(5)	O—N	0.976(9)
Se(2)—O(3)	1.589(5)		
Intermolecular contacts:			
O(2)—Se(2)#2	3.295(5)	O(4)—Se(2)#3	3.010(5)
O(1)#1—Se(1)—O(1)	121.6(5)	O(5)—Se(2)—O(4)	115.8(3)
O(1)#1—Se(1)—O(2)#1	106.1(3)	O(3)—Se(2)—O(4)	116.5(3)
O(1)—Se(1)—O(2)#1	110.1(3)	O(5)—Se(2)—O(2)	102.3(3)
O(1)#1—Se(1)—O(2)	110.1(3)	O(3)—Se(2)—O(2)	97.1(3)
O(1)—Se(1)—O(2)	106.1(3)	O(4)—Se(2)—O(2)	103.5(2)
O(2)#1—Se(1)—O(2)	101.1(4)	Se(1)—O(2)—Se(2)	122.4(3)
O(5)—Se(2)—O(3)	117.1(3)		
Intermolecular angles:			
Se(1)—O(2)—Se(2)#2	117.5(2)	Se(2)—O(4)—Se(2)#3	101.2(2)
Se(2)—O(2)—Se(2)#2	113.2(2)		

Symmetry transformations used to generate equivalent atoms:
#1 −x, y, −z + 1/2
#2 −x, −y, −z
#3 −x − 1/2, −y + 1/2, −z

dry air and inserted in thin-walled quartz capillaries. The intensity data were collected on a KUMA KM-4 four circle kappa-axis diffractometer [19]. An empirical absorption correction based on psi-scan was applied during the data reduction process, T_{max}, T_{min} are 1.000 and 0.306 and 1.000 and 0.310 for **(1)** and **(2)** resp. The structures were solved by direct methods and refined anisotropically by a full-matrix least-squares procedure on F^2. Hydrogen atoms in **(1)** were localized from circular electron density calculations and refined isotropically on the assumption of a "ride-on" model. Atomic parameters of the both structures are presented in the Table 2. The lists of the structure factors and anisotropic temperature coefficients can be obtained upon the request from the author Z. Ž. The programs used were DATAREDX for the data reduction, ABSELI for the absorption correction [20], the structures were solved by SHELXS-86 [21] and refined by SHELXL-93 [22] and the drawings were made by ORTEP [23].

Preparation of Se_3O_7

To 2.8 g of $(SeO_3)_4$ in a Schlenk tube after cooling to −70 °C 25 g of CH_3NO_2 was added. Reaction mixture was warmed to room temperature under vigorous stirring till clear colourless solution formed. Precipitated $Se_3O_7 \cdot CH_3NO_2$ was filtered off after five days and desolvated *in vacuo* at laboratory temperature (100 Pa, 10 hours). Nitrosyl salts of oligoselenic acids were removed by two days' extraction with liquid SO_2 at 50 °C. Yield 1.3 g (51%).

Elemental analysis of Se_3O_7 (348.88): Se^{VI} 23.45 (calc. 22.63)%, Se^{IV} 44.63 (45.27)%. Raman spectrum (see Figure 4, cm^{-1} (rel. int. 1−10)): 1003 Sh(3), 995(4), 972 Sh(6), 964(10), 912(8), 752(2), 725 b(1), 612(2), 520 Sh(3), 502(8), 375(6), 355(4), 300(5), 276(7), 244(8), 215(9), 193(10), 172(7). IR spectrum (cm^{-1} (rel. int. 1−5)): 996 Sh(4), 981(5), 959(5), 909(5), 725 b(5), 665 Sh(3), 611(3), 595(3), 571(3), 542(4), 510(4).

The authors wish to express their gratitude to the Grant Agency of the Czech Republic for the grant No. 203/95/1190

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Address for correspondence:

Doc. Dr. Jiří Toužín
Department of Inorganic Chemistry
Masaryk University
Kotlářská 2
61137 Brno/Czech Republic