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SELENOMALTOL – SYNTHESIS, SPECTROSCOPY AND THEORETICAL CALCULATIONS

Waldemar Tejchman,*[a] Krzysztof Zborowski,[b] Wieslaw Lasocha,[b,c] and Leonard M. Proniewicz[b,d]

[a] Departament of Chemistry, Institute of Biology, Pedagogical University, 2 Podchorazych Str., 30-084 Krakow, Poland

[b] Faculty of Chemistry, Jagiellonian University, 3 Ingardena Str., 30-060 Krakow, Poland

[c] Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, 8 Niezapominajek Str. 30-239 Krakow, Poland

[d] Regional Laboratory of Physicochemical Analysis and Structural Research, Jagiellonian University, 3 Ingardena Str., 30-060 Krakow, Poland

*Corresponding author: 2 Podchorazych Street, 30-084 Krakow, Poland, e-mail address: watejch@ap.krakow.pl

Abstract – Synthesis and structure of the seleno derivative of maltol (selenomaltol) is described. Structural and energetical properties of possible selenomaltol structures have been calculated at the B1LYP/6-311++G(d,p) level. The lowest energies are always predicted for the keto-enol tautomer. To verify obtained results several standard experimental methods, namely: elemental analysis, mass spectrometry, infrared and NMR spectroscopies and X-ray crystallography have been used. Investigation of IR and NMR spectra clearly indicate that the oxygen atom of exocyclic keto group on maltol was replaced by selenium. Experimental crystallographic results support this conclusion.

INTRODUCTION

Maltol (3-hydroxy-2-methyl-4-pyrone) has been widely known as an useful ligand in coordination chemistry.[1] Its metalcomplexes with various metal ions (such as vanadium,[2] oxovanadium,[3] iron[4] and

others) have strong biological activity. Recently, thiomaltol (3-hydroxy-2-methyl-4-thiopyrone), in which the keto oxygen atom is replaced by sulphur[5] was synthetized and used as ligands for metalcomplexes with potential medical (molecular imaging) and environmental (lead ion scavenger) applications.[6,7]

Selenium is an important chemical element. It is one of the trace elements that are essential for human health but are required only in small amounts. In a human body, selenium is incorporated into proteins to form selenoproteins, which are known to be important antioxidant enzymes. The antioxidant properties of selenoproteins help preventing cellular damage from free radicals. Free radicals are natural by-products of oxygen metabolism that may contribute to the development of such diseases as cancer and heart disease.[8,9] Human selenium deficiency is rare but occurs in some countries, most notably in China. Keshan disease (which results in an enlarged heart and poor heart function and occurs in selenium deficient children) is still seen in large areas of the Chinese countryside with selenium poor soil.[10] Hydroxypyrones and hydroxypyridinones are known as non-toxic compounds that can easily penetrate from the digestive system to the blood. Replacement of the oxygen by selenium can be also crucial for creating new useful metalcomplexes. Selenium can modify the solubility and stability of these compounds influencing their medical and environmental activity. All these potential applications of selenomaltol encouraged us to perform this study.

RESULTS AND COMPUTANTIONAL DETAILS

Quantum mechanical calculations have been performed on the B1LYP[11]/6-311++G(d,p)[12] level as implemented in the Gaussian '03 package.[13] The minimum nature of the structures has been confirmed by frequency calculations at the same level of theory. Magnetic properties have been obtained using the GIAO (Gauge Independent Atomic Orbitals) method.[14]

The selenomaltol synthesis was carried out through the direct replacement of the oxygen atom by selenium on treating maltol with phosphorus pentaselenide which had been prepared in situ from red phosphorus and grey selenium.[15] The reaction was performed in xylene under reflux for 12 hours to form dark violet crystal powder. The results of elemental analysis ($C_6H_6O_2Se$) and mass spectrometry [m/z:189 $(MH)^+$] revealed that one oxygen in the maltol molecule was replaced by selenium.

Taking into consideration that there are three oxygens in maltol, three structural isomers were analyzed during the study (Figure 1). They are: isomer A in which the oxygen atom in the keto group is replaced by selenium, isomer B with the oxygen atom of the hydroxyl group being replaced and isomer C in which selenium replaced the oxygen atom in the ring.

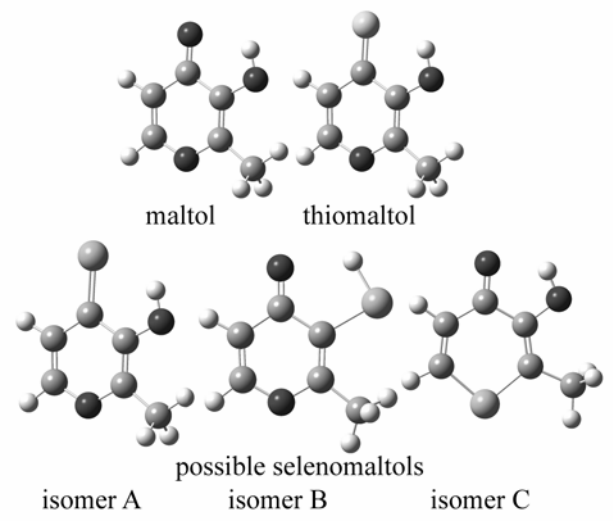

Figure 1. Molecular structures of maltol, thiomaltol and possible selenomaltol isomers A - C

In addition, tautomerism may occur in all these isomers. Tautomeric structures studied in this paper are presented in Figure 2. They are chosen on the base of the previous research on tautomeric equilibria in pyromeconic acid, maltol and ethylmaltol,[16] thiomaltol[17] and kojic acids.[18] Despite the difference in the position of the selenium atom, the tautomers types are the same for all the isomers studied.

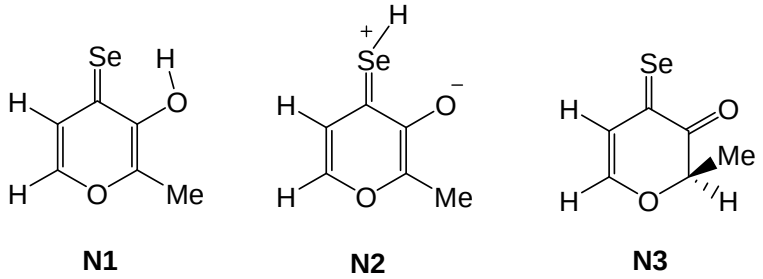

Figure 2. Tautomers of selenomaltol considered for isomer A

Calculated energy gaps and tautomerization reaction constants are collected in Table 1. The data presented clearly demonstrate that the keto-enol tautomer N1 strongly dominates over N2 and N3 in the mixture of tautomers.

In order to recognize the structure of the synthetized compound, the experimental IR spectrum is compared with theoretically predicted spectra calculated for all possible selenomaltol isomers A, B and C. According to the results of tautomeric equilibrium constant calculations, only N1 tautomer is possible. The comparison of theoretical and experimental data (see Figure 3 and Table 2) reveals that under these experimental conditions the oxygen atom of the keto group in maltol is substituted by selenium. First of all, the -O-H stretching vibrational band is present in the experimental spectrum at 3446 cm^{-1}. The presence of this band shows that only structures with the O-H group (substitution of the keto or heterocyclic oxygen) should be considered. For the isomer C, the O-H stretching band according to calculations should be at 3594 cm^{-1}, which is about 150 cm^{-1} higher than in the experiment. In addition,

the pattern of the theoretical spectrum in the C=O and C=C stretching range (about 1700 – 1600 cm^{-1}) is completely different from other isomers.

On the other hand, theoretical spectrum of the tautomer N1 of isomer A fits into experimental data very well. In particular, corresponding band of the C=Se stretching has been found, see Table 2. The differences are not significant in the whole presented spectrum. It is interesting that an insignificant difference is observed even for the –O-H stretching. Such a discrepancy is expected due to the fact that experimental spectrum was measured in the solid state where intramolecular hydrogen bond should be formed. Such hydrogen bonds are observed in maltol[19,20] and thiomaltol[5] crystals. On the other hand, theoretical spectrum was calculated in the one molecule approximation. It suggests that the intermolecular hydrogen bond in the case of selenomaltol is weak. The compatibility of experimental and theoretical spectra could be better after theoretical spectra scaling. This commonly used procedure is based on multiplying calculated frequencies by usually smaller than 1.0 scaling factor.[21] In general, theoretical frequencies are a bit higher than their experimental counterparts so this procedure can diminish the differences between them. Nevertheless, nonscaled theoretical vibrational spectra are presented.

Table 1. Energy gaps (ΔE in kJ/mol, ZPE included) and tautomerization reaction constants for selenomaltol tautomers. Corresponding maltol data[16] are included for comparison.

Tautomers	Maltol	Selenomaltol Isomer 1	Selenomaltol Isomer 2	Selenomaltol Isomer 3
		ΔE		
N1 ↔ N2	49.53	67.17	16.69	46.47
N1 ↔ N3	62.23	67.87	90.81	45.50
		K_T		
N1 ↔ N2	3.46 E-9	1.71 E-12	1.19 E-3	6.66 E-9
N1 ↔ N3	4.27 E-11	1.29 E-12	1.23 E-16	1.07 E-8

Table 2. Characteristic bands of the IR spectra.

	Theory		
Experiment	Isomer 1	Isomer 2	Isomer 3
3446 cm^{-1}, very intensive	O-H stretching at 3450 cm^{-1},very intensive	Se-H stretching at 2357 cm^{-1},intensive	O-H stretching at 3594 cm^{-1}, very intensive
1608 cm^{-1}, very intensive	C=C + C=C in phase stretching at 1667 cm^{-1}, very intensive	C=O stretching at 1698 cm^{-1}, very intensive	C=O + C=C in phase stretching at 1675 cm^{-1}, intensive
1534 cm^{-1}, intensive	C=C - C=C out of phase stretching at 1596 cm^{-1}, very intensive	C=C + C=C in phase stretching at 1670 cm^{-1}, intensive	C=O + C=C in phase stretching at 1644 cm^{-1}, very intensive
1152 cm^{-1}, intensive	C=Se stretching at 1175 cm^{-1}, intensive	C=C - C=C out of phase stretching at 1611 cm^{-1}, intensive	C-Se stretching at 858 cm^{-1}, medium intensity

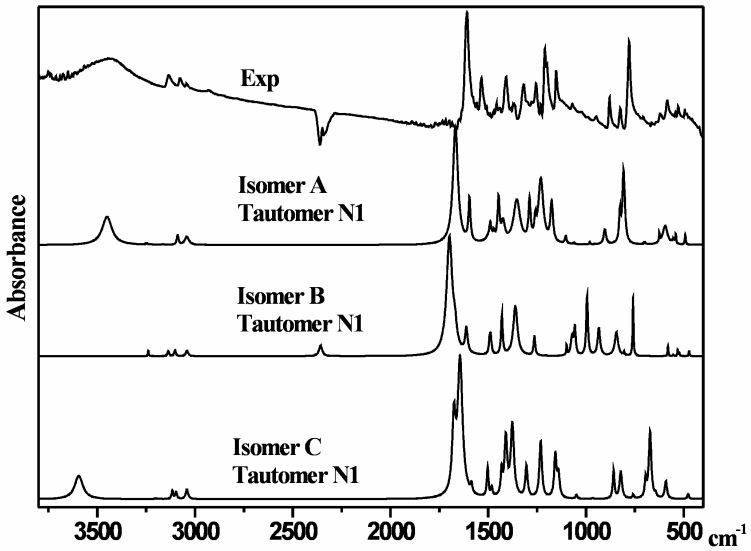

Figure 3. Experimental and theoretical IR spectra.

Nuclear Magnetic Resonance spectroscopy is a very powerful and popular tool for the confirmation of chemical compound structure. In Figure 4 experimental chemical shifts are compared with theoretical predictions for tautomer N1 of the selenomaltol isomer A. The number of signals observed in the experimental ^{1}H and ^{13}C NMR spectra supports the structure proposed by the IR spectroscopy. Also multiplicities in the ^{1}H NMR are the same as those expected for the keto-enol structures with selenium introduced to the keto group. Theoretical and experimental chemical shifts in the ^{1}H NMR are similar. A significant difference is noticed only for the proton of the hydroxyl group. However, a bigger error for this nucleus is reasonable, because hydroxyl group may interact with solvent molecules (DMSO) not included in calculations. It was recently presented that DMSO molecules strongly influence the chemical shifts of labile hydrogens involved in hydrogen bonds.[22] The differences observed between the theoretical and experimental values in the ^{13}C NMR spectroscopy are a bit bigger, but the scale of the carbon chemical shifts range is wider. All experimentally observed signals, except for the carbon atom directly connected with selenium, have their reasonable quality counterparts in theory. On the contrary, a significant error (more than 20 ppm) is observed for the carbon nuclei adjacent to selenium. In this case heavy atom (selenium) influences the shielding of adjacent nucleus. This well described in the literature effect known as “heavy atom effect on the light atom shielding” is caused by spin orbit contribution.[23,24] Such effect is not included in the theory used in this study. If we take that into consideration we can conclude that NMR spectroscopy supported by quantum chemical calculations fully confirmed the proposed structure of the synthetized compound.

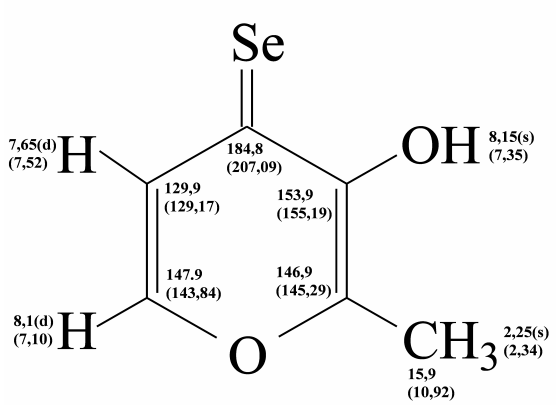

Figure 4. Comparison of theoretical (in parentheses) and experimental NMR shifts for the N1 tautomer of isomer A.

It is interesting to compare the position of signals originating from the protons located at carbon atoms (C-4 and C-5) in maltol, thiomaltol and selenomaltol. Two selenomaltol doublets are present at δ = 7,68 and δ = 8,06 ppm. They are shifted downfield as compared with the analogous signals originating from the protons present in maltol and thiomaltol. The signals from these compounds are present at δ = 6,45 and δ = 7,73 ppm and δ = 7,29 and δ = 7,55 ppm, respectively.[25] Similar behaviour of the protons adjacent to the carbons of the heterocyclic ring under sulphur substitution has been found in the literature in the thiopyranthione derivatives.[26]

The crystal data and the refinement details are listed in Table 3. The structure was solved by direct methods and refined using the SHELXS and SHELXL-97[27] programs. All non-hydrogen atoms were refined anisotropically. The H atoms were located from the difference Fourier maps and refined in idealized positions. Results of the X-ray structural measurements fully support the theoretical and spectroscopic suppositions. The oxygen atom from the keto group is substituted by selenium and selenomaltol exists in the ketoenol form of tautomer N1.

Table 3. Crystal data and structure refinement for selenomaltol.

Identification code	r322
Empirical formula	C6H6O2Se
Formula weight	189.07
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system, space group	MONOCLINIC, P 21/c
Unit cell dimensions	a = 5.511(5) Å alpha = 90.0 deg. b = 8.972(5) Å beta=100.176(5) deg. c = 13.819(5) Å gamma = 90.0 deg.

Volume	672.5(8) Å ^3
Z, Calculated density	4, 1.867 Mg/m^3
Absorption coefficient	5.500 mm^-1
F(000)	368
Crystal size	0.30 x 0.20 x 0.15 mm
Theta range for data collection	3.00 to 30.03 deg.
Limiting indices	-7<=h<=6, -12<=k<=11, -19<=l<=19
Reflections collected / unique	R 6044 / 1968 [R(int) = 0.0218]
Completeness to theta = 30.03	99.8 %
Absorption correction	None
Max. and min. transmission	0.4925 and 0.2892
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1968 / 0 / 88
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0286, wR2 = 0.0697
R indices (all data)	R1 = 0.0399, wR2 = 0.0761
Extinction coefficient	0.0203(19)
Largest diff. peak and hole	0.460 and -0.637 e.A^-3

Selenomaltol crystallizes in the monoclinic system with the following parameters: a = 5.511(5)Å, b = 8.972(5)Å, c = 13.819(5)Å, $\alpha = \gamma = 90°$,$\beta = 100.176(5)^o$, V = 672.5(8)$Å^3$, z = 4, space group $P2_1/c$. The X-ray crystal structure of the investigated compound shows the presence of almost perfectly planar selenomaltol molecules. The rms deviation of O1, C2, C3, C4, C5 and C6 atoms from least squares plane is 0.0075Å, the distance of the O8, H8 or Se atom from this plane is less than 0.0104Å. The atomic parameters and most important inter-atomic distances and angles are presented in Tables 4 and 5. The molecule with numbering scheme and projection of the unit cell of the investigated compound are presented in Figure 5 and 6, respectively. The distance between the Se atom and the C4 atom is 1.825(3)Å. The C3-C4-Se and C5 – C4 –Se angles are $120.79(16)^o$, and $124.03(17)^o$, respectively. The arrangement of atoms: C4, C3, O8, H8 & Se suggests the presence of intramolecular hydrogen bond with O8–Se distance equal to 3.077Å angstroms and O8-H8-Se angle equals 124.52° degrees. Calculated geometrical features are close to the experimental ones, see Table 5.

Table 4. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (A^2 × 10^3) for selenomaltol r322 (U(eq) is defined as one third of the orthogonalized Uij tensor trace).

	x	y	z	U(eq)
Se	9790(1)	4352(1)	6527(1)	49(1)
O(1)	3149(3)	1155(2)	6024(1)	54(1)

O(8)	6444(4)	3447(2)	4591(1)	51(1)
C(3)	5808(4)	2796(2)	5393(2)	38(1)
C(2)	3836(4)	1856(3)	5251(2)	44(1)
C(4)	7161(4)	3082(2)	6348(2)	39(1)
C(5)	6290(5)	2336(3)	7124(2)	49(1)
C(6)	4360(5)	1420(3)	6939(2)	57(1)
C(7)	2268(5)	1497(3)	4297(2)	58(1)

Table 5. Experimental and theoretical bond lengths [Å] and angles [deg] for selenomaltol molecule.

Geometrical parameter	Experiment	Theory (B1LYP/6-311++G(d,p)
Se-C(4)	1.825(3)	1.8286
O(1)-C(6)	1.342(4)	1.3432
O(1)-C(2)	1.350(3)	1.3614
O(8)-C(3)	1.352(3)	1.3462
O(8)-H(8)	0.67(3)	0.9824
C(3)-C(2)	1.362(3)	1.3669
C(3)-C(4)	1.420(3)	1.4411
C(2)-C(7)	1.479(3)	1.4879
C(4)-C(5)	1.417(3)	1.4275
C(5)-C(6)	1.332(4)	1.3512
C(6)-O(1)-C(2)	120.0(2)	120.30
C(3)-O(8)-H(8)	104(3)	106.08
O(8)-C(3)-C(2)	117.7(2)	118.94
O(8)-C(3)-C(4)	120.9(2)	119.99
C(2)-C(3)-C(4)	121.3(2)	121.07
O(1)-C(2)-C(3)	120.2(2)	120.38
O(1)-C(2)-C(7)	113.7(2)	113.31
C(3)-C(2)-C(7)	126.1(2)	126.31
C(5)-C(4)-C(3)	115.2(2)	115.21
C(5)-C(4)-Se	124.03(17)	124.88
C(3)-C(4)-Se	120.79(16)	119.91
C(6)-C(5)-C(4)	120.8(2)	120.49
C(6)-C(5)-H(5)	119.6	119.52
C(4)-C(5)-H(5)	119.6	119.99
C(5)-C(6)-O(1)	122.5(2)	122.55
C(5)-C(6)-H(6)	118.7	125.52
O(1)-C(6)-H(6)	118.7	111.93
C(2)-C(7)-H(7A)	109.5	109.97
C(2)-C(7)-H(7B)	109.5	110.49
H(7A)-C(7)-H(7B)	109.5	109.07
C(2)-C(7)-H(7C)	109.5	110.49
H(7A)-C(7)-H(7C)	109.5	109.07
H(7B)-C(7)-H(7C)	109.5	107.69

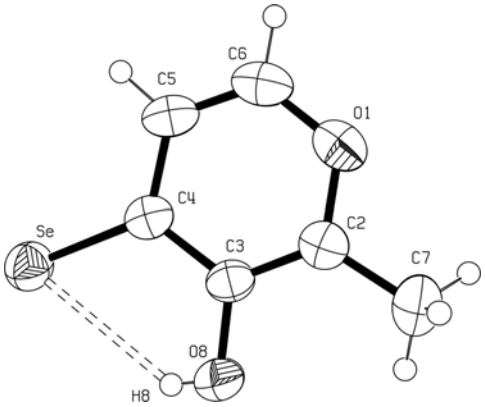

Figure 5. Crystallographic structure and atom numbering scheme of the selenomaltol molecule.

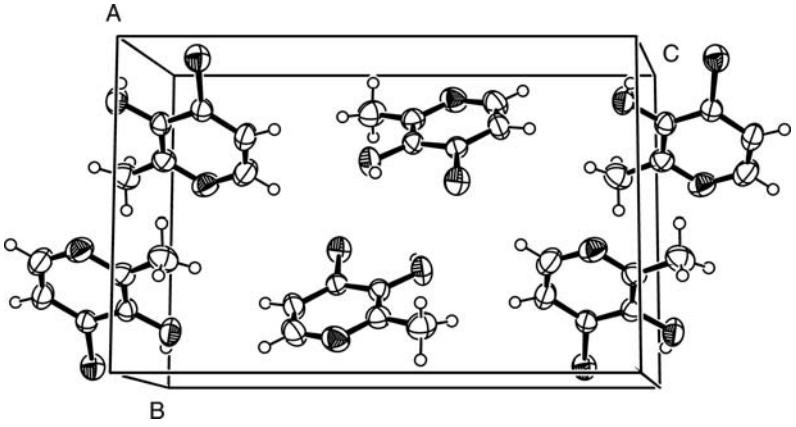

Figure 6. The unit projection of cell.

The investigated selenomaltol is very similar to thiomaltol described earlier.[5] Thiomaltol crystalizes also in the monoclinic system, with very similar lattice parameters (a = 5.3629(4)Å, b = 8.6723(7)Å, c = 13.5524(11)Å, $\beta = 99.858(1)^{o}$, space group also $P2_1/c$).

CONCLUSIONS

The paper describes the synthesis of a new ligand, selenomaltol, with reasonable yield. Elemental analysis and mass spectrometry data revealed that one oxygen atom in maltol was replaced by selenium. The molecular structure of the synthetized compound has been established using some spectroscopic methods (IR and NMR), theoretical calculations and the structural X-ray single crystal analysis. The results of theoretical calculations on the B1LYP/6-311++G(d,p) level shows that among three possible selenomaltol isomers (selenium in the keto group, selenium in the hydroxyl group or selenium in the heterocyclic ring) the most probable is the structure of the keto-enol tautomer. The presence of O-H and C=Se stretching bands in the IR spectrum and high quality similarity of theoretical and experimental spectra prove that selenium is introduced to the keto group. The comparison of experimental ^{1}H and ^{13}C spectra with the

results of chemical shift calculations supports this hypothesis. Finally, the X-ray experiment shows that theoretical and spectroscopic data provide valuable predictions.

Selenomaltol metalcomplexes (similarly to those of maltol and thiomaltol) have numerous possible applications in medicinal and environmental chemistry. Several synthetic reactions of selenomaltol complexes with different metal ions are planned. We believe that selenomaltol tends to be as useful ligand as its oxygen and sulphur counterparts.

EXPERIMENTAL

(Text) Melting point (uncorrected) was determined on a Boetius apparatus. The IR spectrum was recorded with Jasco FT IR-670 Plus spectrophotometer in the KBr disk. The ^{1}H NMR spectra were acquired in DMSO-d_6, at 300 MHz, 25 °C, whereas the ^{13}C NMR spectra were recorded in DMSO-d_6, at 75 MHz, 25 °C, using Varian Mercury – VX 300 MHz spectrometer. The EI MS spectrum at 70 eV was taken with a Finnigan MAT95S instrument. Elementary analyses were carried out with a Perkin Elmer 2400 instrument.

For crystallographic measurements, a single crystal of the investigated compound was picked up and stuck to a glass capillary. The capillary was mounted on the goniometer head and placed in a stream of N_2 vapour. The temperature of the crystal during diffraction experiment was 258K.

The X-ray data for the crystal structure determination were collected on a Kappa CCD Bruker-Nonius diffractometer.

General procedure.

The mixture of maltol 1.26 g (10 mmol), grey selenium 1.975 g (25 mmol) and red phosphorus 0.31 g (10 mmol) in *m*-xylene (25 mL) was refluxed for 12 h. A black precipitate was removed by vacuum filtration. The filtrate was concentrated on a rotary evaporator to give a dark red solid. The solid was recrystalized from *m*-xylene.

Typical yield 27%, melting point 68 ^{o}C. Anal. Calcd. for $C_6H_6O_2Se$: C, 38.12%; H, 3.18%. Found: C, 38.20%; H, 3.15%. This fully confirmed the hypothesis that one oxygen atom in maltol has been replaced by selenium. This conclusion is supported by the results of the mass spectrometry analysis. A molecular ion with the relative intensity of 5.7% was found at m/z = 189. The $[M+1]^+$ ion is the most intensive peak in the mass spectrum. Other intensive peaks are $[M-1]^+$ (relative intensity of 46.5%) and $[C_6H_6O_2]^+$ (selenomaltol molecule without selenium, 28.4%).

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