The synthesis of 1-thia-6-oxa-6aλ^4-seleno-3-azapentalene and a 3*H*-1,2,4-dithiazole†

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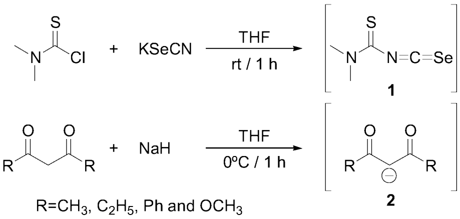
The reaction of thiocarbamoyl isoselenocyanate with a carbanion gave 1-thia-6-oxa-6aλ^4-seleno-3-azapentalene, which has a hypervalent selenium, as the major product. The by-products 3-diacylmethylidene-5-dimethylamino-3*H*-1,2,4-dithiazole and thiocarbamate thioanhydride were also formed.

Introduction

A number of hypervalent organosulfur compounds, sulfuranes, have been reported.[1] In contrast, much less is known about hypervalent organoselenium compounds.[2] The chemistry of hypervalent organoselenium compounds has attracted much attention because of their unusual electronic structure.[3] Organo-chalcogen derivatives with intramolecular interactions are remarkable, providing novel hypervalent, stable organo-selenium[4] or tellurium[5] species with enhanced thermal and hydrolytic stability. However, hypervalent organoselenium compounds of the type C–O–Se–S–C=N have not been investigated and characterized to date, due to difficulties involved in their synthesis.[6] A detailed method for preparation of seleno-3-azapentalene derivatives has not been reported. We have now found that the one-pot reactions of thiocarbamoyl isoselenocyanates with β-diketones afford the corresponding 1-thia-6-oxa-6aλ^4-seleno-3-azapentalene skeleton containing a hypervalent coordinate selenium atom. This is the first example of heterocyclic compounds containing the C–O–Se–S–C=N moiety. We have also confirmed that a rare selenium–sulfur exchange occurs as part of the formation of these compounds.

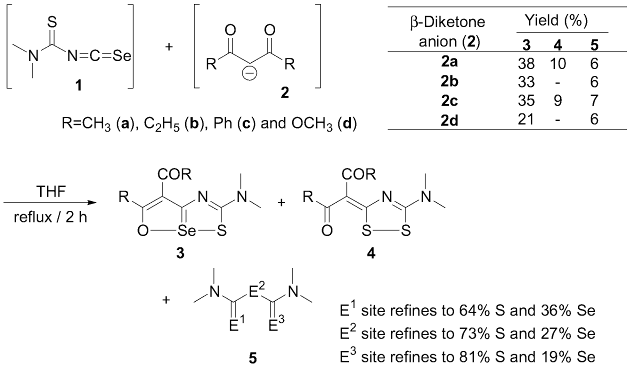
Results and discussion

Recently, isoselenocyanates have been used as starting materials in the synthesis of selenium-containing compounds such as 1,3-selenazoles, 1,3-selenazolidines, 2-phenyl-6*H*-[5,1,3]benzoselenadiazocines, perhydro-1,3-selenazines, 1*H*-5-selena-1,3,6-triazaaceanthrylene and pyrido[1,2-*a*]pyrazines.[7] In order to prepare the 1-thia-6-oxa-6aλ^4-seleno-3-azapentalene skeleton containing a hypervalent selenium atom, we chose thiocarbamoyl isoselenocyanate derivatives (which have C=S and N=C=Se unsaturation), moiety **1**, and carbanion **2** (Scheme 1). Because compound **1** decomposed during silica gel column chromatography, the reaction of carbanion **2** with **1** was carried without purifying **1** by silica gel chromatography.



Scheme 1

The reaction of **1** with **2** gave 1-thia-6-oxa-6aλ^4-seleno-3-azapentalene **3** as the major product. 3-Diacylmethylidene-5-dimethylamino-3*H*-1,2,4-dithiazole **4** and thiocarbamate thioanhydride **5** were obtained as by-products (Scheme 2).



β-Diketone anion (**2**)	Yield (%)		
	3	**4**	**5**
2a	38	10	6
2b	33	-	6
2c	35	9	7
2d	21	-	6

E^1 site refines to 64% S and 36% Se
E^2 site refines to 73% S and 27% Se
E^3 site refines to 81% S and 19% Se

Scheme 2

The structures of compounds **3**, **4** and **5** were fully characterized by IR, ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy, COSY, HMQC and HMBC spectroscopy, and MS and X-ray analysis. To gain more detailed insight into the structural properties of products **3**, **4** and **5**, the compound was subjected to a single crystal X-ray diffraction analysis (Fig. 1).[8]

The bond distances and angles of **3a** fall within the normal range except those involving O5, Se1 and S1, which indicate an attractive interaction between O5 and Se1. A search of the CCDC database (Nov. 2005 version) for structures with the S–Se–C–N(or C)–C cyclic moiety (sp^2 hybridization for the non-chalcogen atoms) yielded four structures with the following average geometries: Se–S = 2.21(2) Å, Se–C = 1.89(2) Å, S–C = 1.78(1) Å;

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† Electronic supplementary information (ESI) available: Complete tables of crystallographic data and ORTEP figures of **3a**, **4a** and **5**. See DOI: 10.1039/b617097h

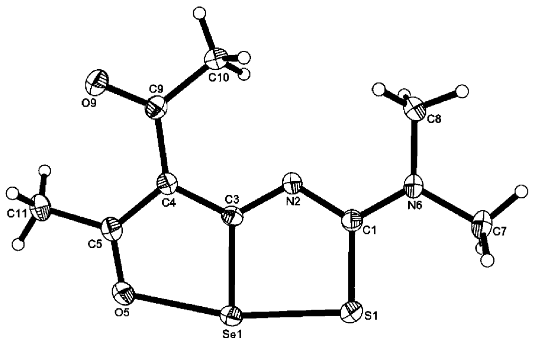


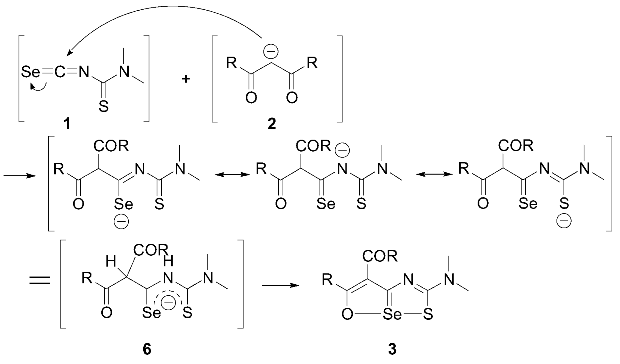
Fig. 1 Thermal ellipsoid plot (35% thermal ellipsoids) of compound **3a**. Selected bond lengths and angles: Se(1)–C(3) 1.9182(17), Se(1)–O(5) 2.1647(13), Se(1)–S(1) 2.3097(6), S(1)–C(1) 1.7348(18) Å; C(3)–Se(1)–O(5) 80.28(6), C(3)–Se(1)–S(1) 86.46(5), O(5)–Se(1)–S(1) 166.70(4), C(1)–S(1)–Se(1) 93.25(6), C(5)–O(5)–Se(1) 110.58(11)°.

C–Se–S = 90.3(9)°, C–S–Se = 96(2)°. Evidence for the O–Se interaction is clear, as the Se1–S1 bond distance is *ca.* five esd units greater that the average value and the S1–Se1–C3 angle is *ca.* four esd units less than the average value. Also, the Se1–C3–C4, C3–C4–C5 and C4–C5–O5 angles are compressed, and the C5–O5 bond is lengthened slightly to accommodate the O5–Se1 interaction. We also note that the O5–Se1 distance (2.1647(13) Å) is significantly shorter than the corresponding O5–S2 distance (2.1968(12) Å) in **4**.

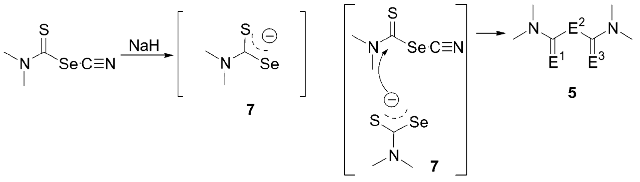
^{1}H NMR spectra of single crystals **3a** showed four methyl groups. In the ^{13}C NMR spectra of single crystals of **3a**, **3b** and **3d**, five carbons (four ring carbons and one carbonyl carbon) are observed in the δ 99–201 range. Furthermore, in the ^{77}Se NMR spectra of **3**, ^{77}Se signals are observed in the δ 976.7 ± 60.9 range, similar to signals from tetravalent selenium compounds (RSeOOH or R_2SeO) (δ 850–1230).[9] These are at lower field than ^{77}Se signals of divalent selenenyl sulfides (RSeSR) (δ 410–660).[10] The data for single crystals of **4** are similar to those for the single crystals of **3**, except for differences in molecular weight, melting points and the lack of the selenium signal in the ^{77}Se NMR spectrum of **4**. Spectra from single crystals of **5** show a mixture of three compounds. In the ^{77}Se NMR spectra of **5**, there are signals at δ 840.8, 912.9 and 916.4. The intensities of the three ^{77}Se signals are consistent with the results from the S–Se substitutional disorder refinement of the X-ray diffraction structure of **5**.

A plausible mechanism for the formation of **3** is initiation by nucleophilic addition of the carbon of the carbanion **2** to the central carbon of the isoselenocyanate **1**, yielding **3** *via* intermediate **6** (Scheme 3). Intermolecular exchange of Se for S in intermediate **6** under reflux conditions would yield compound **4**.

The formation of **5** is explained by the generation of small amounts of thiocarbamoyl selenocyante during the reflux step of the reaction of thiocarbamoyl chloride with potassium selenocyanate to give thiocarbamoyl isoselenocyanate **1**. The thiocarbamoyl selenocyanate transforms into thioselenocarbamate **7**, and the nucleophilic addition of both sulfur and selenium atoms of the anion **7** to the carbonyl carbon of thiocarbamoyl selenocyanate yields **5**, with a mixture of selenium and sulfur isomers (Scheme 4).



Scheme 3



Scheme 4

The chalcogenide exchange reaction of diselenide and trisulfide was studied in solution. Because of the low activation barrier of the selenium exchange reaction, formation of all possible selenium- and sulfur-containing trichalcogenide isomers (–SeSS–, –SSeS–, –SeSeS–, –SeSSe– and –SeSeSe–) were observed.[11] Mixed isomers also form in biological systems in the presence of diselenides and higher sulfides. For example, mixed isomers are formed from cystine (having S–S bonding) and selenocystine having Se–Se bonding.[12] A second example is the exchange of S for Se in the thermolysis of a diselenolatocobalt(III) complex and S_8.[13] In the present reaction, the interesting selenium–sulfur exchange reaction occurs under reflux conditions during the formation of the products.

Conclusions

In conclusion, we have developed a synthesis of the novel 1-thia-6-oxa-6aλ^4-seleno-3-azapentalene skeleton, containing a hypervalent selenium atom.

Experimental

General

The ^{77}Se NMR (95 MHz) spectra were obtained using a JEOL ECA500 spectrometer, and ^{77}Se chemical shifts are expressed in ppm downfield of Me_2Se in $CDCl_3$.

General procedures for the synthesis of compounds 3a, 4a and 5

To a solution of potassium selenocyanate (0.29 g, 2.0 mmol) in anhydrous THF (10 mL) was added thiocarbamoyl chloride (0.25 g, 2.0 mmol) at room temperature under an argon atmosphere. The reaction mixture was stirred at room temperature for 1 h. This solution was added to a solution of $(CH_3CO)_2CH^-$ Na^+ (1.0 mmol) in THF (1.0 mmol, 10 mL), prepared by the reaction of sodium hydride (0.024 g, 1.0 mmol) with acetyl acetone (0.068 g, 1.0 mmol) in dry THF (10 mL) at 0 °C for 0.5 h under an argon atmosphere. The reaction mixture was refluxed for 2 h. The mixture was extracted with diethyl ether and washed with water. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel with diethyl ether–n-hexane (1 : 1) to yield 0.28 g of **3a** (38%), as well as **4a** (10%) and **5** (6%), by flash chromatography on silica gel as yellow crystals.

5-Methyl-2-dimethylamino-4-methylcarbonyl-1-thia-6-oxa-6aλ^4-seleno-3-azapentalene (3a). Mp: 134.9–137.0 °C; IR (KBr): 1387, 1518, 1641 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.55 (3H, s), 2.74 (3H, s), 3.37 (3H, s), 3.48 (3H, s) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ 25.7, 32.4, 41.7, 41.9, 120.5, 182.9, 185.4, 192.1, 197.1 ppm; ^{77}Se NMR (95 MHz, CDCl$_3$): δ 1009.3 ppm; MS (CI): $m/z = 293$ [M$^+$ + 1].

3-Diacetylmethylidene-5-dimethylamino-3*H*-1,2,4-dithiazole (4a). Mp: 109.0–110.5 °C; IR (KBr): 1389, 1534, 1636 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.53 (3H, s), 2.69 (3H, s), 3.29 (3H, s), 3.45 (3H, s) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ 25.8, 32.4, 41.3, 41.9, 118.7, 180.5, 183.9, 192.8, 197.1 ppm; MS (CI): $m/z =$ 247 [M$^+$ + 1].

Thiocarbamate thioanhydride (5). Mp: 109.0–110.5 °C; IR (KBr): 1389, 1534, 1636 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.37, 3.41, 3.42, 3.45, 3.508, 3.513, 3.53, 3.59, 3.60 ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ 43.6, 44.4, 44.8, 45.1, 45.3, 45.8, 47.8, 48.1, 48.8, 186.7, 186.91, 186.95 ppm; ^{77}Se NMR (95 MHz, CDCl$_3$): δ 840.8, 912.9, 916.4 ppm.

5-Ethyl-4-ethylcarbonyl-2-dimethylamino-1-thia-6-oxa-6aλ^4-seleno-3-azapentalene (3b). Mp: 121.2–123.3 °C; IR (KBr): 1640 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.17 (3H, t, $J = 7.5$ Hz), 1.22 (3H, t, $J = 7.5$ Hz), 2.91 (2H, q, $J = 7.5$ Hz), 3.16 (2H, q, $J = 7.5$ Hz), 3.36 (3H, s), 3.46 (3H, s) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ 8.98, 9.96, 30.9, 36.6, 41.5, 41.8, 119.7, 182.6, 184.5, 195.1, 201.2 ppm; ^{77}Se NMR (95 MHz, CDCl$_3$): δ 1005.0 ppm; MS (CI): $m/z = 320$ [M$^+$ + 1].

4-Benzoyl-2-dimethylamino-5-phenyl-1-thia-6-oxa-6aλ^4-seleno-3-azapentalene (3c). Mp: 156.0–157.3 °C, IR (KBr): 1376, 1501, 1641 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.80 (3H, s), 3.16 (3H, s), 7.28 (2H, t, $J = 7.44$ Hz), 7.34 (1H, t, $J = 7.44$ Hz), 7.38 (2H, t, $J = 7.44$ Hz, Ar), 7.47 (1H, t, $J = 7.44$ Hz), 7.59 (2H, d, $J =$ 7.44 Hz), 7.87 (2H, d, $J = 7.44$ Hz) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ 40.5, 41.3, 118.0 128.1, 128.2, 128.3, 129.5, 130.6, 132.2, 136.4, 139.2, 182.0, 183.4, 184.9, 195.1 ppm; ^{77}Se NMR (95 MHz, CDCl$_3$): δ 1007.1 ppm; MS (CI): $m/z = 416$ [M$^+$ + 1].

3-Dibenzoylmethylene-5-dimethylamino-3*H*-1,2,4-dithiazole (4c). Mp: 127.0–128.3 °C, IR (KBr): 1638 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.86 (3H, s), 3.22 (3H, s), 7.29 (2H, t, $J =$ 8.01 Hz), 7.37 (1H, t, $J = 8.01$ Hz), 7.39 (2H, t, $J = 8.01$ Hz, Ar), 7.48 (1H, t, $J = 8.01$ Hz), 7.60 (2H, d, $J = 8.01$ Hz), 7.88 (2H, d, $J = 8.01$ Hz, Ar) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ 40.7, 41.4, 118.2, 128.2, 128.4, 129.7, 130.7, 132.3, 136.5, 139.3, 182.2, 183.6, 185.1, 195.2 ppm; MS (CI): $m/z = 371$ [M$^+$ + 1].

5-Methoxy-4-methoxycarbonyl-2-dimethylamino-1-thia-6-oxa-6aλ^4-seleno-3-azapentalene (3d). Mp: 108.8–110.2 °C; IR (KBr): 1710 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.28 (3H, s), 3.46 (3H, s), 3.85 (3H, s), 3.89 (3H, s) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ 40.8, 42.0, 51.7, 52.8, 99.0, 165.8, 171.8, 180.1, 180.4 ppm; ^{77}Se NMR (95 MHz, CDCl$_3$): δ 885.3 ppm; MS (CI): $m/z = 324$ [M$^+$ + 1].

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8 Single-crystal X-ray diffraction was performed on a Noniu Kappa CCD diffractometer using graphite-monochromated MoKα radiation ($\lambda =$ 0.71069 Å). The structures were solved by direct methods (SHELTXL v5.1, G. M. Sheldrick, Bruker AXS, Inc., Madison, WI, USA, 1997). All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were refined by a riding model. Empirical absorption corrections were applied. CCDC reference numbers: 620570 (**3a**), 620571 (**4a**) and CCDC-620572 (**5**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617097h. Data for **3**: C$_9$H$_{12}$N$_2$O$_2$SSe, FW 291.24, monoclinic, $P2_1/c$, $T = 190(2)$ K, $a =$ 7.6506(8) Å, $b = 18.5206(18)$ Å, $c = 8.4687(8)$ Å, $\beta = 110.451(5)°$, $V =$ 1124.33(19) Å^3, $Z = 4$, $D_c = 1.933$ g cm^{-3}, $\mu = 3.519$ mm^{-1}, crystal size 0.21 × 0.19 × 0.16 mm, data collection range $3.0 < \theta < 27.5°$, limiting indices $-6 \le h \le 9$, $-23 \le k \le 23$, $-10 \le l \le 10$, 13 403 reflections collected, 2517 independent reflections ($R_{\text{int}} = 0.0198$), refined with full-matrix least-squares on F^2, goodness of fit on F^2: 1.078, final R indices

($I > 2\sigma(I)$): $R1 = 0.0224$, $wR2 = 0.0560$, R indices (all data): $R1 = 0.0267$, $wR2 = 0.0582$, largest diff. peak and hole 0.319 and −0.471 e Å^{-3}. Data for **4**: $C_9H_{12}N_2O_2S_2$, FW 244.33, monoclinic, $P2_1/c$, $T = 190(2)$ K, $a = 7.6627(8)$ Å, $b = 18.4638(18)$ Å, $c = 8.3775(8)$ Å, $\beta = 110.288(5)°$, $V = 1111.74(19)$ Å^3, $Z = 4$, $D_c = 1.460$ g cm^{-3}, $\mu = 0.46$ mm^{-1}, crystal size 0.40 × 0.10 × 0.06 mm, data collection range $2.8 < \theta < 27.5°$, limiting indices $-9 \le h \le 9$, $-23 \le k \le 23$, $-10 \le l \le 10$, 31 420 reflections collected, 2537 independent reflections ($R_{int} = 0.0249$), refined with full-matrix least-squares on F^2, goodness of fit on F^2: 1.031, final R indices ($I > 2\sigma(I)$): $R1 = 0.0320$, $wR2 = 0.0802$, R indices (all data): $R1 = 0.0412$, $wR2 = 0.0845$, largest diff. peak and hole 0.315 and −0.215 e Å^{-3}. Data for **5**: $C_6H_{12}N_2O_2S_{1.96}Se_{1.04}$, FW 257.01, monoclinic, $P2_1/c$, $T = 190(2)$ K, $a = 10.1624(10)$ Å, $b = 7.4766(7)$ Å, $c = 14.1240(14)$ Å, $\beta = 111.027(5)°$, $V = 1001.68(17)$ Å^3, $Z = 4$, $D_c = 1.704$ g cm^{-3}, $\mu = 4.237$ mm^{-1}, crystal size 0.41 × 0.24 × 0.14 mm, data collection range $3.1 < \theta < 27.5°$, limiting indices $-13 \le h \le 13$, $-9 \le k \le 9$, $-18 \le l \le 18$, 29 933 reflections collected, 2293 independent reflections ($R_{int} = 0.0180$), refined with full-matrix least-squares on F^2, goodness of fit on F^2: 1.143, final R indices ($I > 2\sigma(I)$): $R1 = 0.0236$, $wR2 = 0.0475$, R indices (all data): $R1 = 0.0277$, $wR2 = 0.0486$, largest diff. peak and hole 0.266 and −0.300 e Å^{-3}.

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