

HYPERCOORDINATED ORGANOSELENIUM COMPOUNDS WITH O→Se INTRAMOLECULAR INTERACTIONS

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ABSTRACT. Single-crystal X-ray diffraction studies revealed a monomeric structure with O→Se intramolecular coordination in compounds [Me₂C(OH)CH₂][2-(Me₂NCH₂)C₆H₄]Se (**1**) and [2-(O=CH)C₆H₄]Se[S(S)P(OPrⁱ)₂] (**2**). These interactions result in distorted T-shaped coordination geometries around selenium in both compounds and prevent a C,N-chelating behavior of the 2-(Me₂NCH₂)C₆H₄ group in **1** and a bidentate behaviour of the dithiophosphorus ligand in **2**, respectively.

Keywords: organoselenium compounds; intramolecular coordination; solid state structure; dithiophosphato ligands.

INTRODUCTION

A continuously increased interest was observed during last years for main group organometallic compounds bearing organic groups with pendant arms capable for intramolecular E→M (E = O, N; M = main group metal or metalloid) interactions, mainly due to the specific properties induced by such an interaction, e.g. increased thermal and hydrolytic stability or adjustable conformation rigidity [1,2]. In most cases, the use of functionalized aromatic groups with potential for intramolecular coordination results in chelate species stabilized in a monomeric form. Such compounds proved to be valuable candidates in catalysis, medicine or materials science, as they display

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improved catalytic properties, biological activity or thermal behavior than the species without such intramolecular interactions [3,4]. In organoselenium compounds the N→Se intramolecular interaction was observed to reduce the Lewis acidity and to increase the electrophilic reactivity of the chalcogen atom, thus making it more suitable for additional Se→M coordination. In this way, organoselenium compounds bearing organic groups with potential for building hypercoordinated species become useful multidentate ligands using both hard (O, N) and soft (Se) donor atoms [5-10].

During the last years our research interest was focused on organoselenium compounds with organic groups of type 2-(R₂NCH₂)C₆H₄ (R = Me, Et, Prⁱ) [11-14], 2,6-(R₂NCH₂)C₆H₃ [15], (RN=CH)C₆H₄ (R = Bn, Mes, Ph) [16] or 2-(O=CH)C₆H₄ [17] groups, as well as several metal complexes, either metal organoselenolates [18-20], or compounds bearing the alkoxy functionalized ligands, [R₂C(OH)CH₂](2-Me₂NCH₂C₆H₄)Se [21]. As a continuation of our studies we discuss here the crystal and molecular structure of two organoselenium(II) compounds with potential for hypercoordination, namely [Me₂C(OH)CH₂](2-Me₂NCH₂C₆H₄)Se (**1**) and [2-(O=CH)C₆H₄]Se[S₂P(OPrⁱ)₂] (**2**), with emphasis on the intramolecular E→Se (E = N, O) possible interactions.

RESULTS AND DISCUSSION

We described previously the synthesis and the solution behavior of compounds [Me₂C(OH)CH₂](2-Me₂NCH₂C₆H₄)Se (**1**) [21] and [2-(O=CH)C₆H₄]Se[S₂P(OPrⁱ)₂] (**2**) [17], but at that time we didn't succeed to obtain single crystals suitable for X-ray diffraction studies.

Single-crystal X-ray diffraction studies

The molecular structures of compounds **1** and **2** were determined by single-crystal X-ray diffraction. The ORTEP-like diagrams with the atom numbering schemes for compounds **1** and **2** are displayed in Figures 1 and 2, respectively, while important interatomic distances and angles are given in Tables 1 and 2, respectively.

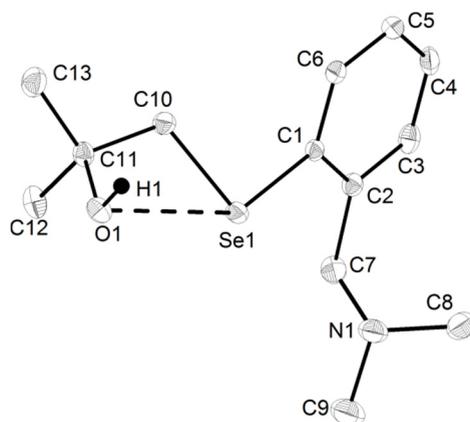


Figure 1. ORTEP-like diagram at 30% probability for compound **1**. Hydrogen atoms, except H1 were omitted for clarity.

Table 1. Selected interatomic distances [Å] and angles [°] in **1**.

Se1–C1	1.928(4)		C1–Se1–C10	98.20(18)
Se1–C10	1.967(4)		C1–Se1...O1	146.48(13)
Se1...O1	3.121(3)		C10–Se1...O1	50.71(13)

Both compounds have monomeric structures with a distorted T-shaped coordination geometry around selenium ($O1\cdots Se1-C1$ 146.48° in **1** and $O1\cdots Se1-S1$ 176.10° in **2**) and chelate rings, *i.e.* four-membered SeC_2O in **1** and five-membered SeC_3O in **2**, respectively. In compound **1** the nitrogen-selenium interatomic distance (3.44 Å) is just at the limit of the sum of the van der Waals radii of the two elements [Σr_{vdW} (N,Se) 3.54 Å] [22], while typically such interactions were observed in the range $2.358(2)$ - $3.135(3)$ Å in other related species, *i.e.* $[2-(Me_2NCH_2)C_6H_4]_2Se_2$, $[2-(Me_2NCH_2)C_6H_4]_2Se$ [23] or $[2,6-(Me_2NCH_2)C_6H_3]Se^+$ [15]. The OH hydrogen atom is not involved in any intra- or intermolecular interaction. This contrasts with the phenyl substituted analogue $[Ph_2C(OH)CH_2][2-(Me_2NCH_2)C_6H_4]Se$, where a strong $N\cdots H-O$ interaction of 2.03 Å [Σr_{vdW} (N,H) 2.74 Å] is established [21]. In compound **1** the $N1\cdots H1$ interatomic distance is much greater (6.51 Å) than the sum of the van der Waals radii of these two elements. This behavior can be explained by the constraint determined by the intramolecular $O\rightarrow Se$ interaction ($Se1\cdots O1$ 3.12 Å) [*cf.* Σr_{vdW} (O,Se) 3.40 Å] [22], which prevents any further participation of the OH hydrogen to hydrogen bonding.

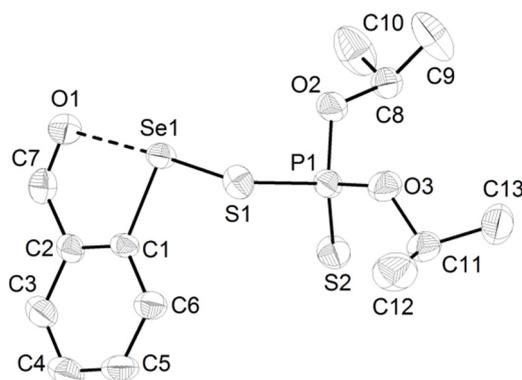


Figure 2. ORTEP-like diagram at 30% probability for compound **2**. Hydrogen atoms were omitted for clarity.

Table 2. Selected interatomic distances [Å] and angles [°] in **2**.

Se1–C1	1.934(4)		C1–Se1–S1	101.41(14)
Se1–S1	2.216(1)		C1–Se1...O1	76.50(15)
Se1...O1	2.575(4)		S1–Se1...O1	176.10(10)
P1–S1	2.0865(16)			
P1–S2	1.9087(19)			

In compound **2** the O→Se intramolecular interaction of 2.575 Å is similar with that one found in [2-(O=CH)C₆H₄]Se[S(S)PPh₂] (2.568 Å) and much stronger than the sum of the van der Waals radii of oxygen and selenium. The dithiophosphorus ligand is coordinated in a monodentate fashion to selenium, with single P–S [P1–S1 2.086(2) Å] and double P=S [P1–S2 1.908(2) Å] bonds [cf. P–S 2.077(1) and P=S 1.954(1) Å in Ph₂P(S)SH] [24]. These values are similar with those found in the related [2-(O=CH)C₆H₄]Se[S(S)PPh₂] [17] or the compounds of type [2-(iPr₂NCH₂)C₆H₄]Se[S(S)PR'₂] (R' = Ph, OPr) [13].

CONCLUSIONS

The single-crystal X-ray diffraction studies revealed the presence of O→Se intramolecular interactions in the monomeric species [Me₂C(OH)CH₂](2-Me₂NCH₂C₆H₄)Se (**1**) and [2-(O=CH)C₆H₄]Se[S(S)P(OPr)₂] (**2**). In compound **1** the intramolecular O→Se coordination pushed the nitrogen atom in the pendant arm of the 2-(Me₂NCH₂)C₆H₄ group away from the coordination sphere of selenium, thus preventing any intramolecular N→Se interaction, while in compound **2** the intramolecular C=O→Se interaction determines a monodentate monoconnective behavior of the organophosphorus ligand.

EXPERIMENTAL SECTION

X-ray structure determination

The details of the crystal structure determination and refinement for compounds **1** and **2** are given in Table 3. Data were collected on a Bruker SMART APEX diffractometer by using graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). The crystals were attached with paratone/N oil on cryoloops. The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used [25]. The drawings were created with the Diamond program [26].

Table 3. Crystal data and structure refinement for $[\text{Me}_2\text{C}(\text{OH})\text{CH}_2][2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{Se}$ (**1**) and $[2-(\text{O}=\text{CH})\text{C}_6\text{H}_4]\text{Se}[\text{S}(\text{S})\text{P}(\text{OPr}^i)_2]$ (**2**)

	1	2
Empirical formula	$\text{C}_{13}\text{H}_{21}\text{NOSe}$	$\text{C}_{13}\text{H}_{19}\text{O}_3\text{PS}_2\text{Se}$
Formula weight	286.27	397.33
Temperature (K)	150(2)	293(2)
Wavelength (\AA)	0.71073	0.71073
Crystal system	Tetragonal	Monoclinic
Space group	I-4	C2/c
<i>a</i> (\AA)	19.9049(12)	28.106(5)
<i>b</i> (\AA)	19.9049(12)	8.0787(13)
<i>c</i> (\AA)	7.0189(8)	16.977(3)
α ($^\circ$)	90	90
β ($^\circ$)	90	114.002(3)
γ ($^\circ$)	90	90
Volume, (\AA^3)	2780.9(5)	3521.5(11)
<i>Z</i>	8	8
Density (calculated) (g/cm^3)	1.367	1.499
Absorption coefficient (mm^{-1})	2.682	2.463
<i>F</i> (000)	1184	1616
Crystal size, mm	0.30 x 0.25 x 0.19	0.20 x 0.22 x 0.38
θ range for data collections, $^\circ$	1.447 to 24.929	1.60 to 25.00
Reflections collected	13389	16308
Independent reflections	2445 [$R_{\text{int}} = 0.0484$]	3099 [$R_{\text{int}} = 0.049$]
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2445 / 0 / 150	3099 / 0 / 185
Goodness-of-fit on F^2	1.037	1.172
Final <i>R</i> indices [$ I > 2\sigma(I)$]	$R_1 = 0.0274$ $wR_2 = 0.0588$	$R_1 = 0.0536$ $wR_2 = 0.1144$
<i>R</i> indices (all data)	$R_1 = 0.0288$ $wR_2 = 0.0593$	$R_1 = 0.0649$ $wR_2 = 0.1192$
Largest diff. peak and hole, $\text{e}\text{\AA}^{-3}$	0.355 and -0.188	0.751 and -0.261

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SUPPLEMENTARY DATA

CCDC 1587750 and 1571839 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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