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The structural characterisation of telluraphthalic anhydride, selenaphthalic anhydride and of 2-selenaphthalide

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Abstract

The characterisation, by single crystal X-ray methods, of three heterocyclic organoselenium and -tellurium compounds is reported. Tellura phthalic anhydride (**1**), $C_8H_4O_2Te$, and selenaphthalic anhydride (**2**), $C_8H_4O_2Se$, are both monoclinic and crystallise in space group $P2_1/n$. 2-Selenophthalide (**3**), C_8H_6OSe, is also monoclinic, space group $P2_1/c$. The Te(Se)–C(sp^2) bond lengths in **1**, **2**, and **3**, averaging at 2.161(6) Å (Te) and 1.945(1) Å (Se) are longer than observed normally (2.116 and 1.893 Å, respectively). No evidence of electron delocalisation in the heterocyclic rings of **1** and **2** is noted; however, a short C(8)–C(7) bond and a relatively long C(8)=O bond in **3** indicates some degree of delocalisation in that case. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In a recent series of papers [1–4] it has been demonstrated that the reaction of heterocyclic selenium and tellurium compounds with dodecacarbonyl triiron [1,3,4], or with rhodium derivatives [2], under relatively mild conditions may afford novel organometallic compounds. In some cases dechalcogenation occurs giving metallocyclic compounds or materials in which novel organic fragments are stabilised by co-ordination to the metal. In other cases the reaction stops prior to that step and the products are based on molecules formed by the insertion of the transition metal into the heterocyclic moiety. A comparison of similar organoselenium and -tellurium heterocyclic compounds is proving valuable [4] in probing the several steps in the complex dechalcogenation reactions, since the sulfur analogues are often less reactive under similar conditions [1,5,6].

It is desirable that the heterocyclic organochalcogen compounds used in the above investigations are totally characterised, hence in this short paper we report the characterisation, by single crystal X-ray methods, of three materials which were subjected to reactions with dodecacarbonyl triiron [4], namely telluraphthalic anhydride [7], 2-selenaphthalide [8], and selenaphthalic anhydride [7].

2. Experimental

Telluraphthalic anhydride [7], 2-selenaphthalide [8] and selenaphthalic anhydride [7] were prepared using the indicated literature methods. All manipulations involving reactions of tellurium and selenium compounds were carried out under an atmosphere of pure argon with the use of Schlenk techniques. TLC (purity check) was carried out on UV active silica gel plates.

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Table 1
Crystallographic data

Compound	**1**	**2**	**3**
Formula	$C_8H_4O_2Te$	$C_8H_4O_2Se$	C_8H_6Ose
M	259.7	211.1	197.1
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	8.534(4)	8.529(3)	7.809(4)
b (Å)	5.849(4)	5.748(3)	6.403(3)
c (Å)	15.528(5)	15.349(4)	15.038(5)
β (°)	100.73(1)	104.07(1)	99.83(2)
U (Å^3)	761.5(7)	729.9(5)	740.9(6)
Z	444		
$D_{calc.}$ (g cm^{-3})	2.265	1.921	1.767
μ(Mo–K$_\alpha$) (mm^{-1})	3.84	5.08	4.99
θ range (°)	2.7–25.2	2.7–25.2	2.6–25.2
Reflections collected [$I>\sigma(I)$]	3763	4086	3531
Unique reflections	1283	1254	1216
R_{int}	0.0369	0.1204	0.0818
Variables refined	100	100	92
Δ/σ(max)	0.001	0.001	0.002
$\Delta\rho$ (e Å^{-3})	0.52, −0.81	0.98, −0.54	0.51, −0.73
R, wR_2 [a]	0.0577, 0.1245	0.0593, 0.1467	0.0989, 0.1724
Observed reflections [$I>2\sigma(I)$]	1173	1184	1035
R, wR_2 [a] observed data	0.0514, 0.1204	0.0562, 0.1434	0.0768, 0.1551
w (a,b) [b]	0.052, 1.83	0.081, 0.25	0.079, 0

[a] $wR_2 = [\Sigma\, w(F_o^2 - F_c^2)^2 / \Sigma\, w(F_o^2)^2]^{1/2}$.

[b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bp]$ where $P = (F_o^2 + 2F_c^2)/3$.

3. Crystallographic analysis

Crystal parameters and experimental data are listed in Table 1. Cell dimensions and intensity data for the three structures were measured on a Rigaku R-AXIS II area detector diffractometer at 293(2) K using graphite-monochromated Mo–K$_\alpha$ radiation, $\lambda = 0.7107$ Å. The structures were determined [9] by direct methods and refined [10] by least-squares on F^2 using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed in calculated positions, riding on their respective bonding atoms. Diagrams were drawn with ORTEP [11]; thermal ellipsoids are at the 30% probability level.

Atomic co-ordinates, thermal parameters and full lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

4. Discussion

Views of the molecules telluraphthalic anhydride (**1**), selenaphthalic anhydride (**2**) and 2-selenaphthalide (**3**) are shown in Figs. 1–3. Selected geometric parameters are listed in Table 2.

Tellurium and selenium to sp^2-hybridized carbon bond lengths are longer than normally accepted values, averaging 2.161(6) and 1.945(1) Å, respectively, compared with 2.116 and 1.893 Å given in the tabulations of Allen et al. [12] There is little evidence of electron delocalisation in the phthalic anhydrides, **1** and **2**; however in **3**, a short C(8)–C(7) bond and a relatively long C(8)=O bond appear to indicate some degree of delocalisation.

Although the non-hydrogen atoms of the three molecules are each essentially coplanar, rms atomic deviations 0.021 Å (**1**), 0.035 Å (**2**) and 0.018 Å (**3**), closer examination reveals some small but significant deviations from true planarity. In **1**, the phenyl ring is planar to within ±0.008 Å, rms deviation 0.005 Å, with the bonded carbon atoms displaced on opposite

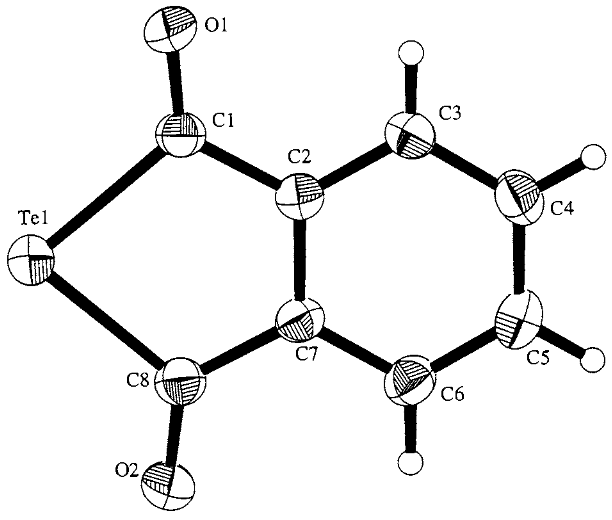

Fig. 1. View of complex **1**.

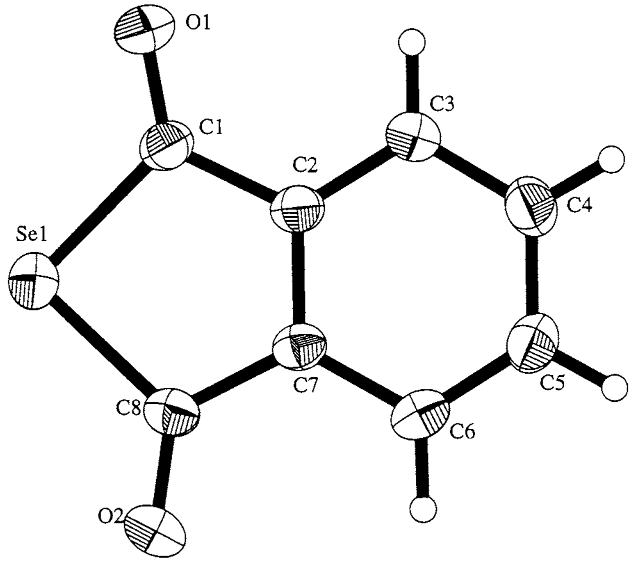

Fig. 2. View of complex **2**.

sides of the phenyl plane by 0.033 and 0.049 Å, and their respective carbonyl oxygen atoms displaced in the same directions by 0.055 and 0.101 Å. The tellurium atom lies close (0.009 Å) to the phenyl plane. In **2**, the phenyl ring is again planar, rms atomic deviation 0.002 Å, C(1), C(8) and the selenium atom are displaced by, respectively 0.009, 0.032 and 0.130 Å on the same side of this plane, with carbonyl oxygen O(1) lying 0.043 Å on the opposite side of the phenyl plane and O(2) lying close (0.006 Å) to the plane. 2-Selenaphthalide (**3**) has the eight carbon atoms essentially coplanar (maximum atomic deviation 0.005 Å, rms deviation 0.003 Å) with the selenium and carbonyl oxygen atoms deviating by

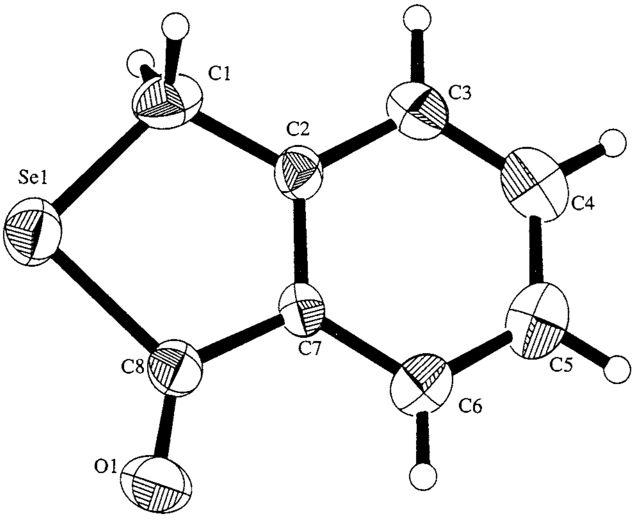

Fig. 3. View of complex **3**.

0.037 and 0.054 Å on opposite sides of the carbon-atom plane.

The near-planarity of these complexes, and of thiophthalic anhydride [13] and the parent, phthalic anhydride [14], notwithstanding the differences in bond lengths involving the hetero-atoms, 2.161 Å in telluraphthalic anhydride (**1**), 1.945 Å in selenaphthalic anhydride (**2**), 1.801 Å in thiophthalic anhydride [13] and 1.395 Å in phthalic anhydride [14] (Table 2) is made possible by the flexibility of valence angles within the five-membered ring. Thus while the C–O–C angle in phthalic anhydride is close to normal at 109.5°, the corresponding angles in thiophthalic anhydride, and complexes **2** and **1** are 92.6(2), 87.3(2) and 81.5(3)°, respectively, correlating with the longer bond lengths.

Table 2
Selected bond lengths (Å) and angles (°) with estimated S.D. in parentheses

	1	**2**	**3**		
	X = Te	X = Se	X = Se	X = S[a]	X = O[b]
Bond lengths (Å)					
X–C(1)	2.166(7)	1.945(5)	1.958(9)	1.801(6)	1.393(5)
X–C(8)	2.155(7)	1.946(5)	1.944(8)	1.801(4)	1.396(4)
C(1)–O	1.198(8)	1.197(6)		1.200(7)	1.192(5)
C(8)–O	1.210(9)	1.209(6)	1.224(10)	1.194(8)	1.192(4)
C(1)–C(2)	1.483(9)	1.483(6)	1.486(11)	1.482(5)	1.471(3)
C(8)–C(7)	1.489(10)	1.473(6)	1.456(10)	1.479(7)	1.466(4)
C(1)···C(8)	2.820(10)	2.687(6)	2.706(11)	2.605(7)	2.277(4)
Bond angles (°)					
C(1)–X–C(8)	81.5(3)	87.3(2)	87.8(4)	92.6(2)	109.5(3)
X–C(1)–C(2)	110.5(5)	110.0(3)	108.5(6)	109.8(4)	107.6(3)
X–C(8)–C(7)	110.8(5)	110.3(3)	110.3(6)	109.3(4)	107.6(3)
C(1)–C(2)–C(7)	118.7(6)	116.0(4)	117.0(7)	113.4(5)	107.8(3)
C(8)–C(7)–C(2)	118.4(6)	116.2(4)	116.4(7)	114.7(4)	107.4(3)
Σ (angles)	539.9	539.8	540.0	539.8	539.9

[a] Previous work [2].

[b] Previous work [3].

Similarly the angle at selenium in 2-selenophthalide (3) is 87.8(4)°. This large decrease in angle at the heteroatom in going from O to S to Se to Te is accompanied by concomitant increases in the angles C(1)–C(2)–C(7) and C(8)–C(7)–C(2). These angles range from 107.6° in phthalic anhydride to 118.5° in telluraphthalic anhydride (Table 2). There is also a small increase in the angles at the carbonyl carbon atoms. The net result of these bond angle variations is that the sum of the angles within the five-membered ring is, in each case, within 0.2° of 540°, the required value for a planar ring.

There are no exceptionally short intermolecular contacts. The closest contacts involving tellurium are Te···O, 3.375 Å and Te···Te, 3.828 Å (cf. van der Waals distances of 3.58 and 4.12 Å, respectively [15]). In the selenium complexes, the closest Se···Se intermolecular distances are 3.889 Å in **2** and 4.050 Å in **3** (the van der Waals distance is 3.80 Å). In **2** there is also an Se···O contact distance of 3.413 Å (cf. van der Waals distance, 3.42 Å).

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