

Crystal Structure of the β -Clathrate Form of 4-*p*-Hydroxyphenyl-2,2,4-trimethylselenachroman

D. D. MACNICOL*, P. R. MALLINSON, R. A. B. KEATES, and F. B. WILSON
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

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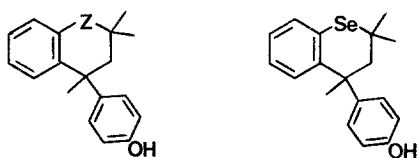
Abstract. In contrast to *p*-hydroxyphenyl-2,2,4-trimethylchroman, Dianin's compound (**1**), or its *thia* analogue **2**, the title seleno-ether has been found to form two crystallographically distinct types of clathrate. In the first-discovered form, the α -modification of as yet undefined structure, the rhombohedral unit cell ($R\bar{3}$, $a = 57.42(1)$ Å, $c = 10.817(1)$ Å, [from EtOH]) has approximately four times the volume of that found in the clathrates of **1** or **2** and contains 72 host molecules. Recrystallisation of the seleno-host from *n*-hexane, however, produces another type of rhombohedral crystal: the β -modification has space group $R\bar{3}$, with $a = 28.225(2)$ Å, $c = 10.859(1)$ Å, and 18 host molecules in the unit cell. A detailed X-ray study of this latter inclusion compound (host-guest ratio 6 : 1) has established its true clathrate nature; the disordered *n*-hexane guest, showing electron density consistent with an extended planar zig-zag conformation, is found threading the hour glass-shaped cavity's central constriction.

Key words: Inclusion Compounds; X-ray crystal structure analysis; *p*-Hydroxyphenyl-2,2,4-trimethylselenachroman host; two clathrate forms; detailed study β -form, guest *n*-hexane.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82045 (25 pages).

1. Introduction

The ability of *p*-hydroxyphenyl-2,2,4-trimethylchroman (**1**), commonly known as Dianin's compound, and its thiachroman analogue **2** to form parallel series of isomorphous and isostructural clathrates is now widely recognised [1]. Taking as an example the ethanol



(1) $Z = O$, (2) $Z = S$ (3)

clathrates, space group $R\bar{3}$, one finds similar lattice parameters $a = 26.97$, $c = 10.99$ Å; and $a = 27.81$, $c = 10.90$ Å respectively for **1** and **2** for a hexagonal unit cell containing 18 host and 6 ethanol guest molecules: in each case, almost identical cages are available for guest accommodation [2, 3]. The present work is concerned with the inclusion properties of 4-*p*-hydroxyphenyl-2,2,4-trimethylselenachroman (**3**), prepared [4] analogously to its thiachroman counterpart **2**, and provides the first detailed structural information for an inclusion compound of this selenoether host. Interestingly, host **3** exhibits a new feature not

found for **1** or **2**; namely that the number of crystallographically independent host molecules is dependent upon the nature of the guest species included. Recrystallisation of **3** from ethanol produces an inclusion compound (host-guest ratio 3 : 1, by 200 MHz ^1H n.m.r.), space group $R\bar{3}$, with a unit cell, $a = 57.42(1)$ Å and $c = 10.817(1)$ Å (referred to hexagonal axes) which has approximately four times the volume of that found for the clathrates of **1** or **2**. Since this form of **3**, which has four crystallographically distinct host molecules, was discovered first for this selenoether host it is referred to as the α -form. This form is currently under further detailed study. Subsequently discovered, a second modification, the β -form, was found to crystallise from *n*-hexane, this hydrocarbon guest being incorporated with a host-guest ratio of 6 : 1 determined by 200 MHz ^1H n.m.r. The present work describes a detailed X-ray study of the β -form which is also trigonal, space group $R\bar{3}$ with $a = 28.225(2)$ Å and $c = 10.859(1)$ Å (hexagonal axes) for a unit cell containing 18 host and 3 *n*-hexane guest molecules.

2. Experimental

Prepared as described previously [4] the new seleno-ether host **3** gave m/e 332.0681 ($\text{C}_{18}\text{H}_{20}\text{OSe}^{80}$ requires 332.0679). The 200 MHz ^1H n.m.r. spectrum (δ , CDCl_3) comprised signals (3H each) at δ 1.19, 1.57, and 1.78 (the first quoted [CMe_2] resonances have prominent Se^{77} satellites; $|^3J_{\text{Se}, \text{H}}|$ 14.4 and 13.1 Hz respectively); an AB spectrum (2H) centred at δ 2.28 (δ_{AB} 0.30 ppm; $|J|$ 14.5 Hz) from the nonequivalent methylene hydrogens; an AA' BB' spectrum (4H) centred at δ 6.83 from the ring protons of the *p*-hydroxyphenyl group, and an ABCD spectrum (4H, in range δ 7.0–7.4) from the remaining aromatic hydrogens; and finally a concentration-dependent signal (1H, *ca.* δ 4.5 in dilute solutions) from the phenolic OH proton. Adducts of **3** were prepared by recrystallisation of **3** from the appropriate pure, dry solvent.

Table I. Fractional atomic coordinates and isotropic temperature factors (angstrom squared), with standard deviations in the least significant digits in parentheses. For anisotropic atoms, the equivalent isotropic temperature factors are shown.

Atom	x/a	y/b	z/c	U	Atom	x/a	y/b	z/c	U
C(2)	0.11791(14)	-0.10290(14)	-0.59533(31)	0.054	C(21)	0.0000	0.0000	-0.5598(18)	0.181(7)
C(3)	0.10721(16)	-0.15232(14)	-0.51770(33)	0.052	C(22)	0.0221(11)	0.0191(12)	-0.6728(23)	0.138(9)
C(4)	0.13889(14)	-0.14528(13)	-0.39820(30)	0.048	O	0.06966(12)	-0.05001(12)	-0.02144(26)	0.060
C(5)	0.2345(2)	-0.1185(2)	-0.3284(4)	0.080	Se	0.13992(2)	-0.26411(2)	-0.67849(4)	0.070
C(6)	0.2907(2)	-0.0910(3)	-0.3354(5)	0.094	H(3A)	0.2206(16)	-0.1581(16)	-0.7607(43)	0.05(1)
C(7)	0.31617(18)	-0.05768(22)	-0.43307(52)	0.082	H(3B)	0.263(2)	-0.164(2)	-0.826(5)	0.08(2)
C(8)	0.28550(19)	-0.05180(19)	-0.52373(51)	0.072	H(5)	0.1103(18)	-0.1992(19)	-1.0623(47)	0.06(1)
C(9)	0.22775(14)	-0.07995(14)	-0.51645(34)	0.055	H(6)	0.308(3)	-0.091(3)	-0.305(6)	0.10(2)
C(10)	0.20087(15)	-0.11440(15)	-0.41608(31)	0.054	H(7)	0.355(2)	-0.041(2)	-0.438(5)	0.08(1)
C(11)	0.12157(13)	-0.11882(13)	-0.29541(29)	0.045	H(8)	0.2973(19)	-0.0362(18)	-0.5839(43)	0.05(1)
C(12)	0.15789(13)	-0.07040(13)	-0.23400(31)	0.046	H(12)	0.1402(14)	-0.2816(15)	-1.0731(33)	0.038(9)
C(13)	0.13986(14)	-0.04874(14)	-0.14295(32)	0.049	H(13)	0.1730(16)	-0.3127(16)	-1.2279(35)	0.05(1)
C(14)	0.08605(14)	-0.07378(13)	-0.11092(30)	0.049	H(15)	0.3221(19)	-0.1951(18)	-1.1764(41)	0.07(1)
C(15)	0.04890(14)	-0.12220(15)	-0.16969(36)	0.056	H(16)	0.0441(18)	-0.1740(19)	-0.2967(43)	0.06(1)
C(16)	0.06736(14)	-0.14307(15)	-0.25971(36)	0.055	H(17A)	0.081(2)	-0.230(2)	-0.360(5)	0.08(2)
C(17)	0.1208(2)	-0.2045(2)	-0.3568(4)	0.069	H(17B)	0.1984(18)	-0.1297(17)	-1.0613(43)	0.06(1)
C(18)	0.1097(2)	-0.0601(2)	-0.5290(4)	0.076	H(17C)	0.203(2)	-0.112(2)	-0.924(5)	0.07(1)
C(19)	0.0822(3)	-0.1226(3)	-0.7105(5)	0.088	H(18A)	0.193(2)	-0.290(2)	-0.867(5)	0.08(1)
C(20)	0.000	0.000	-0.786(3)	0.217(9)	H(18B)	0.264(2)	-0.256(2)	-0.829(5)	0.09(2)
					H(18C)	0.1113(17)	-0.0350(17)	-0.6054(39)	0.06(1)
					H(19A)	0.282(3)	-0.210(3)	-0.620(7)	0.13(3)
					H(19B)	0.244(3)	-0.241(2)	-0.549(5)	0.10(2)
					H(19C)	0.083(2)	-0.146(3)	-0.744(6)	0.09(2)
					H(O)	0.0438(17)	-0.0673(17)	-0.0079(37)	0.04(1)

CRYSTAL DATA $6[\text{C}_{18}\text{H}_{20}\text{OSe (3)}] \cdot \text{C}_6\text{H}_{14}$: $M = 2074.10$, trigonal, $R\bar{3}$, $a = 28.225(2)$, $c = 10.859(1) \text{ \AA}$, $V = 7492(1) \text{ \AA}^3$, $Z = 3$, $D_c = 1.38 \text{ g cm}^{-3}$, $\mu = 30.7 \text{ cm}^{-1}$ for $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). $T = 293 \text{ K}$.

Some 3168 independent X-ray intensity measurements, comprising all possible reflections with $\sin \theta/\lambda < 0.61 \text{ \AA}^{-1}$, were made by θ - ω scan on a Nonius CAD4 diffractometer from a single crystal having dimensions $0.7 \times 0.7 \times 0.2 \text{ mm}$ sealed in a thin-wall glass capillary. The intensities were corrected for absorption effects by an empirical method [5]. The principal computer programs used in structure solution and refinement are listed in reference [5]. During the anisotropic least-squares refinement hydrogen atoms were located in difference-Fourier maps and their isotropic parameters included in subsequent refinement. The hydrogen atoms of the statistically-disordered *n*-hexane guest could not, however, be located. The final R factor for 2654 reflections with $F^2 > 2\sigma(F^2)$ is 0.049, R' 0.066. Atomic coordinates and displacement parameters are given in Tables I and II (Table II has been deposited with the British Library under Supplementary Publication No. SUP 82045.)

3. Discussion

Figure 1 shows a general view of the host molecule **3** in its *n*-hexane inclusion compound. The heterocyclic ring of **3** has a distorted half chair conformation. Displacements of C(2) and

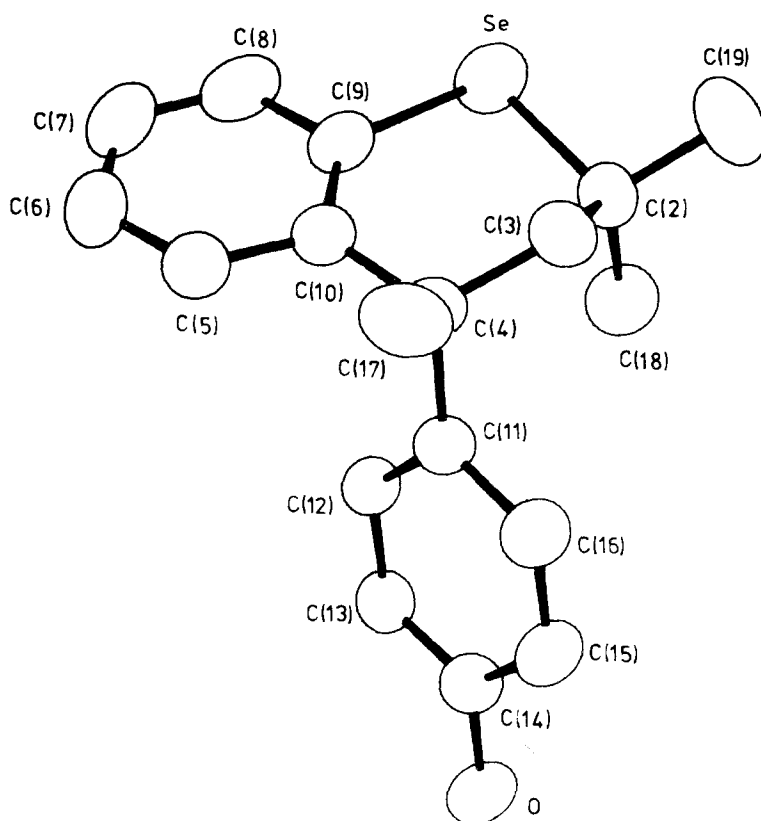


Fig. 1. A general view illustrating the structure of the host molecule 4-*p*-hydroxyphenyl-2,2,4-trimethylselenachroman (**3**) in its *n*-hexane clathrate.

C(3) of, respectively, -0.33 and 0.39 Å from the mean plane defined by atoms Se, C(9), C(10), and C(4) may be compared with the corresponding pairs of displacements of $-0.29, 0.38$ Å; $-0.38, 0.35$ Å for **1** and **2** (for the unsolvated form and the 2,5,5-trimethylhex-3-yn-2-ol clathrate respectively.) In **3** the torsion angle C(16)–C(11)–C(4)–C(3), $+57^\circ$, relates to corresponding values for **1** and **2** of $+60^\circ$ and $+58^\circ$.

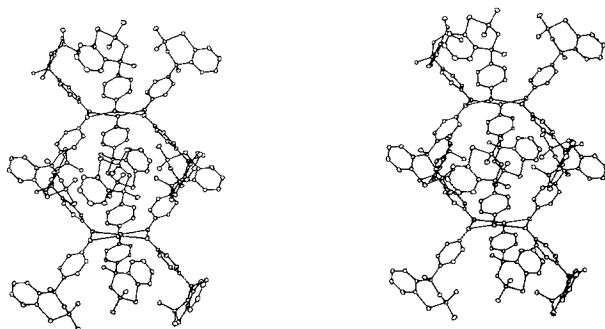


Fig. 2. A stereoview normal to the *c*-axis illustrating the host packing of 4-*p*-hydroxyphenyl-2,2,4-trimethylselenachroman (**3**).

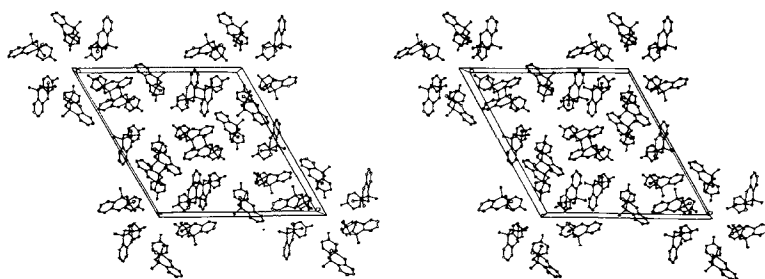


Fig. 3. A stereoview looking down the *c*-axis showing the unit cell of the *n*-hexane clathrate of 4-*p*-hydroxyphenyl-2,2,4-trimethylselenachroman (**3**).

Figures 2 and 3 illustrate the host structure of **3**, which is closely related to Dianin's compound **1** [6], and to its thia-analogue **2** [7]. In the host structure of **3**, groups of six molecules are linked by hydrogen bonds involving the hydroxyl groups such that the oxygens form a distorted hexagon, molecules of opposite configuration lying alternately on opposite sides of its mean plane. Two such groups of 6 molecules of **3** are stacked along the *c*-axis such that their bulkier parts interlock, forming a cage. The O...O hexamer dimension in **3** is $2.975(3)$ Å and the displacements of the oxygen atoms from the mean plane are ± 0.24 Å. The *c*-spacing for the *n*-hexane adduct of **3** is $10.859(1)$ Å compared to a value of 10.990 Å for the 2,5,5-trimethylhex-3-yn-2-ol clathrate of **2**. As may be seen from the stereoview (Figure 2), six methyl groups, one from each of six host molecules, are located near the centre of the cage shown. These methyl groups give rise to a central constriction at $z = \frac{1}{2}$ of *ca.* 4.4 Å diameter. Accordingly, as for **1** and **2**, the cage again possesses an hour-glass-shaped cavity contour extremely similar to that found in the clathrates of 4-*p*-hydroxy-2,2,4-trimethylthiachroman **2** [3, 7] and Dianin's compound itself [2, 8].

Three independent electron density peaks arise from the guest molecule, the molecular centre of which is located at $0,0,\frac{1}{2}$. The central and terminal carbons lie close to the *c*-axis and, as a result of statistical disorder involving the three positions about the axis, only an average position, exactly on the *c*-axis, is found for each of these two atoms. The intramolecular separation of the terminal methyl groups, 6.22(4) Å indicates that the molecule possesses an essentially planar zig-zag conformation. A corresponding distance of 6.45(1) Å has been found independently [9] in the molecular crystal of *n*-hexane at -115°C , where the molecule again exhibits a planar, extended *trans* conformation.

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