Synthesis, Crystal Structure and Photoluminescence of 1,2-Bis(phenylselenyl)-1,2-dicarba-*closo*-dodecaborane(12)

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The reaction of dithio-*o*-carborane with diphenyldiselenide (PhSeSePh) affords the title compound, *closo*-1,2-$(PhSe)_2C_2B_{10}H_{10}$ (**1**), which has been characterized by IR and NMR (^{1}H, ^{11}B) spectroscopy and by single-crystal X-ray diffraction. The phenylselenyl groups are bonded to the cage carbon atoms of the *o*-carborane cluster with a C_{cage}–C_{cage} distance of 1.751(6) Å and an Se–C_{cage}–C_{cage}–Se torsion angle of 10.1(3)°. Compound **1** displays a violet emission on excitation with UV light. For comparison the photoluminescence of the known analog *closo*-1,2-$(PhS)_2C_2B_{10}H_{10}$ (**2**) was also studied.

Key words: Diphenyldiselenide, *o*-Carborane, Synthesis, Crystal Structure, Photoluminescence

Introduction

There has recently been considerable interest in functionalized carborane clusters. One direction of this field lies in the study of carborane cluster ligands (especially those based on *o*-carborane or *closo*-$C_2B_{10}H_{12}$) and their metal coordination compounds [1, 2], utilizing the excellent thermal, oxidative and chemical stability and the many potential applications imparted by the carborane moieties [3, 4]. Besides the well-known metallacarborane clusters [2], the ligand systems combining the *o*-carborane skeleton and functional groups such as cyclopentadienyls [5, 6], phosphines [7 – 11] and Si/Sn [12] or S/Se heteroatoms [13, 14] *etc.* have received much current interest. On the other hand, *o*-carborane has been shown to be a good system to modulate the C–C distance [15, 16]. Depending on the steric and electronic nature of the C-substituents, the carbon-carbon distances within the C_2B_{10} clusters can vary from 1.629(4) Å in *closo*-$C_2B_{10}H_{12}$ [17] to 2.156(4) Å in a sterically crowded ferrocenyl derivative reported recently [18].

In 2002 Viñas *et al.* [19] described the synthesis and structure of *closo*-1,2-$(PhS)_2C_2B_{10}H_{10}$, in which the C_{cage}–C_{cage} distance (1.799(3) Å) was found to be considerably longer than that in *o*-carborane. Although many metal complexes containing 1,2-dithio- or 1,2-diseleno-*o*-carborane moieties have been reported, organic selenium-containing derivatives are relatively rare [20 – 26]. To further study the properties of this type of functionalized compounds and the substituent effect on the carbon-carbon distances in the *o*-carborane skeleton, we have prepared the title compound and herein report on its synthesis, crystal structure and photoluminescence.

Results and Discussion

The reaction of dilithio-*o*-carborane with PhSeSePh gave the colorless compound **1** (Scheme 1) in high yield. **1** was characterized by IR, ^{1}H and ^{11}B NMR spectroscopy. The IR spectrum of **1** shows the characteristic B–H stretching at 2586 cm^{-1}. In the ^{1}H NMR spectrum of **1**, the signals for the phenyl groups are observed as a multiplet at 7.184 – 7.743 ppm and for the B-bound protons at 1.582 – 2.564 ppm. The ^{11}B NMR spectrum exhibits broad signals at −2.8, −8.6 and −10.8 ppm.

The solid-state structure of **1** has been established by an X-ray diffraction analysis (Fig. 1). Single crystals were grown from an ether solution of **1** at room temperature. Details of the crystal parameters, data collection and refinement are summarized in Table 1, and selected bond lengths and bond angles are given in Table 2. As shown in Fig. 1, the structure has crystallographic C_2 symmetry with the two-fold axis bisecting the C7–C7^i and B3–B3^i bonds. The two PhSe groups directly bonded to the cage carbon atoms are

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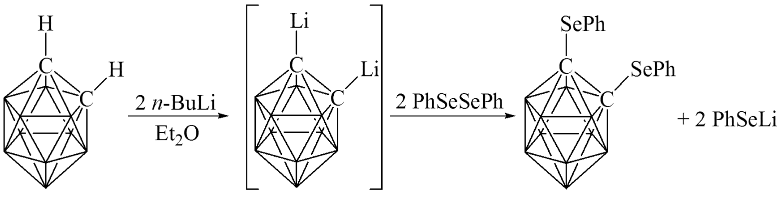

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Scheme 1. The synthesis of compound **1** (undefined vertices represent BH).

Table 1. Crystal data and data collection and refinement details for **1**.

Formula	$C_{14}H_{20}B_{10}Se_2$
M_r	454.32
Crystal size, mm^3	0.25 × 0.20 × 0.10
Temperature, K	298(2)
Crystal system	monoclinic
Space group	*C*2/*c*
a, Å	20.353(7)
b, Å	8.801(3)
c, Å	11.919(4)
β, deg	112.542 (6)
V, Å^3	1972.0 (12)
Z	4
D_{calcd}, g cm^{-3}	1.53
μ(MoK_α), mm^{-1}	3.7
F(000), e	888
hkl range	$-26 \le h \le +14$
	$-10 \le k \le +11$
	$-14 \le l \le +15$
θ range, deg	2.17 ~ 27.46
Refl. total / unique / R_{int}	5399 / 2208 / 0.045
Refl. observed [$I \ge 2\,\sigma(I)$]	1761
Data / restraints / ref. parameters	2208 / 0 / 138
*R*1 / *wR*2 [$I \ge 2\,\sigma(I)$][a]	0.0460 / 0.1131
*R*1 / *w*R2 (all data)	0.0602 / 0.1219
$(\Delta/\sigma)_{max}$	0.000
GoF (F^2)[b]	1.046
$\Delta\rho_{max/min}$, e Å^{-3}	1.31 / −0.60

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o)^2 + (0.076P^2) + 0.0P]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$;
[b] GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

pointing outwards with respect to the cage (the Se–C7–C7^i–Se^i torsion angle is 10.1(3)° and the C1–Se–C7 angle is 102.13(13)°) thus minimizing the repulsion of the electron lone pairs at the selenium atoms. The Se–C bond lengths (1.931(3) and 1.921(3) Å) are identical within experimental error, similar to those reported [13, 20–26] for *o*-carborane derivatives with direct C$_{cage}$–Se bonds. The cage C–C bond (1.751(6) Å) is longer than those found in the *o*-carborane parent (1.629(4) Å) [17] and in an *exo*-polyhedral diselenacyclohexene derivative (1.634(5) Å) [21], but somewhat shorter than those in the sulfur analogs 1,2-(PhS)$_2$-*closo*-$C_2B_{10}H_{10}$ (**2**) (1.799(3) Å) [19] and 1,2-(CH$_3$S)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (1.8033(18) Å) [27].

Table 2. Selected bond lengths (Å) and angles (deg) for **1** with estimated standard deviations in parentheses[a].

Se–C1	1.921(3)	C7–B1^i	1.715(4)
Se–C7	1.931(3)	C7–B1	1.722(5)
C7–B4	1.688(5)	C7–C7^i	1.751(6)
C7–B5	1.692(5)		
C1–Se–C7	102.13(13)	C7^i–C7–Se	119.12(9)

[a] Symmetry code: (i) $-x$, y, $-z$+3/2.

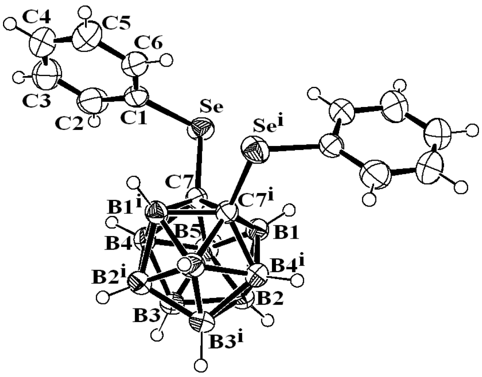

Fig. 1. Molecular structure of **1** in the crystal, with crystallographic atom numbering; displacement ellipsoids for non-hydrogen atoms are at the 50 % probability level.

The Se··· Se^i distance of 3.643(11) Å is slightly shorter than the sum of the van der Waals radii of Se (3.80 Å), but considerably longer than the corresponding sum of the covalent radii (2.340 Å), indicating no bonding interaction between the two Se atoms. In the present structure there exist no significant intermolecular interactions.

It is believed that the significant elongation of the C$_{cage}$–C$_{cage}$ distance in **1** compared with that in *closo*-$C_2B_{10}H_{12}$ is the result of both electronic and steric effects as described for its sulfur analogs [15, 19], and the difference (from that in compound **2**) may be attributed to the difference in electronegtivity between sulfur (2.58) and selenium (2.55, both Pauling scale) atoms.

The UV/Vis absorption spectrum of **1** in chloroform shows a maximum at 243 nm, with very weak vibrational bands at *ca.* 266 and 273 nm, suggesting

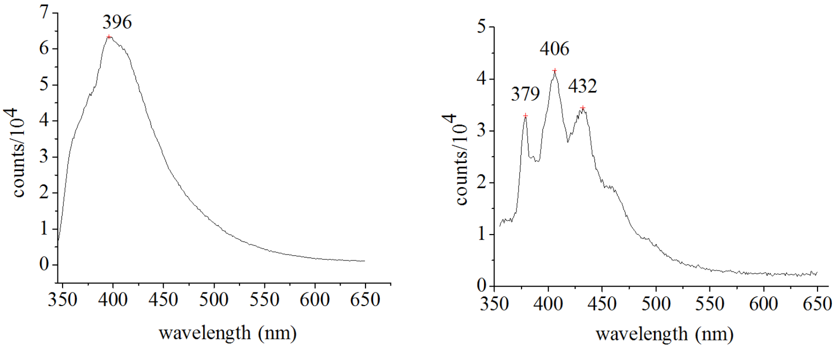

Fig. 2. Fluorescence spectra of **1** (left) and **2** (right) in chloroform.

that there is essentially no conjugation between the carborane nucleus and the PhSe substituent groups, which is in accord with the data described for some phenylcarboranes [28]. The photoluminescence of **1** in chloroform solution was investigated at r. t. As shown in Fig. 2, compound **1** exhibits a violet emission band with the maximum around 396 nm on excitation with UV light (λ_{ex} = 337 nm). For comparison, the photophysical properties of the sulfur analog 1,2-$(PhS)_2$-*closo*-$C_2B_{10}H_{10}$ (**2**) (prepared according to ref. 19) was also studied in chloroform solution at r. t. The UV/Vis spectrum of compound **2** shows an absorption maximum at 240 nm, with significant vibrational structure at around 258 nm. As can be seen in Fig. 2, compound **2** displays a similar emission band centered at 406 nm (λ_{ex} = 340 nm), but again with more significant vibrational structures when compared with that of compound **1**.

Experimental Section

Analytically pure reagents were commercially available. The IR spectrum was recorded on a Perkin Elmer Spectrum RX I spectrometer in the range 400 – 4000 cm^{-1} using a KBr pellet. UV/Vis spectra were recorded on a TU-1900 UV/Vis spectrometer. NMR analysis was performed on a Bruker Avance 400 MHz spectrometer with tetramethylsilane (TMS) as internal standard (^1H) and $BF_3 \cdot OEt_2$ as external standard (^{11}B). Fluorescence analysis was performed on a FLS920 spectrometer. The melting point was measured with a SGW X-4 apparatus, and the temperature was not corrected.

*Synthesis of **1***

Under an Ar atmosphere, a solution of *n*-BuLi (2.2 M in hexane, 0.85 mL, 1.87 mmol) was added *via* syringe to a solution of *closo*-$C_2B_{10}H_{12}$ (134 mg, 0.93 mmol) in diethyl ether (15 mL) at 0 °C. The resulting suspension was stirred for 30 min at 0 °C and an additional 30 min at r. t., and then cooled to 0 °C before a solution of PhSeSePh (581 mg, 1.86 mmol) in diethyl ether (25 mL) was added. The mixture was stirred at 0 °C for 30 min, and then for 30 min at r. t. before it was quenched with an aqueous NaCl solution. The organic phase was separated and the water phase extracted with ether. The combined organic phases were washed with brine and dried over $MgSO_4$ to give a yellowish solid. Recrystallization in ether afforded compound **1** as colorless crystals (367 mg, 87 %). M. p. 175 – 178 °C. – UV/Vis ($CHCl_3$): λ_{max} (ε_{max}) = 243 nm (2686 L · mol^{-1} · cm^{-1}). – IR (KBr): ν = 3063, 2924, 2586 (B–H), 1474, 1438, 738 cm^{-1}. – ^1H NMR (400.1 MHz, $CDCl_3$, 292.7 K): δ = 7.184 – 7.743 (m, 10H, CH_{Ph}), 1.582 – 2.564 (br, 10H, BH). – ^{11}B NMR (128.4 MHz, $CDCl_3$, 292.8 K): δ = −2.8, −8.6, −10.8.

Crystal structure determination

A suitable crystal of **1** was selected and mounted on a Bruker SMART APEX II CCD diffractometer for data collection (graphite-monochromatized MoK_α radiation (λ = 0.71073 Å), ω scan mode). The structure was solved by Direct Methods and expanded using Fourier difference techniques with the SHELXTL-97 program package [29]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. Hydrogen atoms on the phenyl rings were placed in geometric positions, the B-bound hydrogen atoms were added on the difference Fourier map, and all were refined isotropically.

CCDC 726075 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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