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A soluble molecular variant of the semiconducting silicondiselenide†

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Silicondiselenide is a semiconductor and exists as an insoluble polymer (SiSe₂)_n which is prepared by reacting elemental silicon with selenium powder in the temperature range of 400-850 °C. Herein, we report on the synthesis, isolation, and characterization of carbene stabilized molecular silicondiselenide in the form of (cAAC)₂Si₂Se₄ (3) [cAAC = cyclic alkyl(amino)carbene]. 3 is synthesized *via* reaction of diatomic silicon(0) compound (cAAC)₂Si₂ (2) with black selenium powder at -78 °C to room temperature. The intensely orange colored compound 3 is soluble in polar organic solvents and stable at room temperature for a month under an inert atmosphere. 3 decomposes above 245 °C. The molecular structure of 3 has been confirmed by X-ray single crystal diffraction. It is also characterized by UV-vis, IR, Raman spectroscopy and mass spectrometry. The stability, bonding, and electron density distributions of 3 have been studied by theoretical calculations.

Introduction

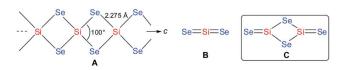
The synthesis of silicon diselenide (SiSe₂; **A** in Scheme 1) was first reported by P. Sabatier in 1891.¹ Six decades later crystalline SiSe₂ was prepared by Weiss *et al.*² who reported the Bravais lattice of the crystal structure of SiSe₂ as body-centered orthorhombic. Structural analysis showed that it crystallizes in space group *Ibam.*³a-b SiSe₂ has a unique crystalline structure which consists of infinite nonintersecting chains of edge-sharing tetrahedra (**A**) as shown in Scheme 1.³a-b The structural scenario of amorphous SiSe₂ is more complicated,³c where the Si atoms are linked *via* intra- and inter-tetrahedral bonds connected by Se atoms. The predominant structural motif of amorphous SiSe₂ follows the sequence involving both corner- and edgesharing connections,³c which are importantly more frequent than those constructed exclusively by edge-sharing Si atoms in crystalline SiSe₂.³a-b

quest of the physical properties of $SiSe_2$ in a single phase. Large red rods of $SiSe_2$ have been grown for 4–7 days inside a quartz tube at $1000\,^{\circ}$ C under high vacuum placed in a furnace.^{4–6} They are highly moisture sensitive and undergo hydrolysis on the surface to produce silicon- and selenium dioxide.⁴ The glass transition temperature and crystallization temperature of $SiSe_2$ are 460 and 610 $^{\circ}$ C, respectively.⁵ Further studies showed that $SiSe_2$ can exist as three different polymorphs depending upon the temperature (400–850 $^{\circ}$ C) of preparation.⁶ Crystalline $SiSe_2$ is considered to be a semiconductor^{4,7a–b} and has a huge potential to be used in solar cells.^{7c}

Several modified synthesis routes have been developed in

After the first synthesis report of N-heterocyclic carbenes (NHCs) in 1991, they have been utilized as strong σ -donating ligands in different areas of chemistry. The mono-atomic and diatomic variants of silicon are stabilized by NHCs and cAACs in form of L: \rightarrow Si(0) = Si(0) \leftarrow :L, and L: \rightarrow Si(0) \leftarrow :L [L: = NHC or cAAC (cyclic alkyl(amino)carbene)]. Several variants of phosphorus are stabilized by NHCs and cAACs, respectively. G. Bertrand *et al.* have stated that carbene stabilized variants of these elements are synthesized not only for academic curiosity but also for their solubility in organic solvents. Since organic ligand-anchored variants are more soluble in organic

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Scheme 1 Schematic representation of some forms of SiSe₂.

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Scheme 2 Synthesis of compound 3 from 2. The energy term in parenthesis is ΔG (kcal mol $^{-1}$) at M06-2X/TZVP/SMD//M06-2X/SVP level of theory for 2a to 3a.

solvents, their chemical transformations are much easier and faster. They are suggested to be utilized for the synthesis of the smaller units of the larger framework/polymer such as silicon dioxide (Si₂O₄).¹⁰ Very recently, the syntheses and characterizations of (NHC)₂Si₂O₃ and (NHC)₂Si₂O₄ were reported by Robinson et al. 12a Reaction of (NHC)2Si2 with excess of oxygen donor (N2O or O2) led to the isolation of free NHC and uncharacterized decomposed product of silicon oxide. The light yellow colored (NHC)₂Si₂O₃ was isolated only when three equivalents of N2O are allowed to react with (NHC)2Si2. Note, that (NHC)₂Si₂O₃ does not convert to higher oxide analogue (NHC)2Si2O4 when the former compound is further reacted with N2O. The synthesis of colorless compound (NHC)2Si2O4 is successful only when (NHC)2Si2 is reacted with two equivalents of molecular oxygen (O2).12a Y. Apeloig has summarized the compounds containing Si=O double bonds giving high emphases on NHC stabilized Si₂O₃ and Si₂O₄ oxides. 12b However, monomeric or dimeric variants of SiSe₂ (B, C; Scheme 1) in the molecular form are even not reported by low temperature matrix-isolation. Herein, we report on the synthesis and characterization of carbene-stabilized (SiSe₂)₂ in the molecular form of (cAAC)₂Si₂Se₄ (3). The reaction employed cAAC-supported diatomic silicon(0) (cAAC)2Si2 (2) which is reacted with black selenium powder in the temperature range of -78 °C to rt (Scheme 2). Moreover, the stability and bonding of 3 are studied by theoretical calculations.

Result and discussion

Both cAAC and NHC form stable adducts with SiCl₄.9a,c The colorless adducts (cAAC) → SiCl₄ (1a, Me₂-cAAC; 1b, Cy-cAAC) are obtained when cAACs react with $SiCl_4$ in 1 : 1 molar ratio in THF. 15a,9c The diatomic silicon(0) (cAAC)2Si2 (2a-b) has been synthesized by complete dechlorination of 1 with four equiv of KC_8 in THF (see ESI†). 2a-b are isolated as dark black-purple needles from *n*-hexane solution (see ESI for details, Schemes S1–S2†). The yield of 2a is 52% which is higher than that of red colored (NHC)₂Si₂ (21%)^{9a} but comparable to that of 2b.^{9c} Theoretical calculation showed that cAAC is more firmly bound to the Si₂ unit and thus 2 is even characterized by EI-mass spectrometry, or while its NHC analogue (NHC)₂Si₂ is not. The latter species dissociates under such conditions and only free NHC is found in the mass spectrum. This is due to the weaker π accepting property¹³ which makes NHC-containing compounds more labile.14

(NHC)₂Si₂, 9a and (cAAC)₂Si₂ (2a, Me₂-cAAC; 2b, Cy-cAAC) are studied by solid state ²⁹Si NMR at room temperature (rt) to compare the electronic environments of the silicon atoms. (NHC)₂Si₂ shows its ²⁹Si resonance at 202.4–204.3 ppm which is close to the corresponding value of 224.5 ppm (singlet) in solution.94 Analogous measurement on 2a exhibits a singlet at 254.6 ppm, while two resonances (190.1 and 318.3 ppm) are observed for 2b. Note, that the calculated (190.1 + 318.3)/2 =254.2] mean value is \sim 254 ppm. There is no resonance around 254 ppm in the solid state ²⁹Si NMR of 2b suggesting that the two silicon atoms are not equivalent. The changes in the chemical shift values of NHC and cAAC derivatives are attributed to the higher π -accepting property of cAAC over NHC.¹⁶ However, the reason behind the two well separated (128.2 ppm) ²⁹Si resonances in **2b** is not apparently understood. The temperature dependent X-ray single crystal studies revealed that both 2a and 2b crystallize in the triclinic $P\bar{1}$ space group. The center of inversion in between the two silicon atoms in 2b is absent at 100 K (see ESI†), but it is present at 23 K.9c In comparison, the center of inversion in between the two silicon atoms in 2a is present even at 100 K (see ESI†). Structural comparison between 2a and 2b clearly shows that the carbene moieties are evenly disordered in 2a but not in 2b (Fig. S5-S8†). The combined solid state NMR and temperature dependent Xray structural correlation unambiguously clarify the acute differences of electronic environments of silicon atoms in 2a-b. In the solution phase both 2a and 2b have a similar coordination environment and hence their 29Si resonances are close to each other (252.3 ppm for 2a and 249.1 ppm for 2b) (Schemes S5-S6, Fig. S12-S13, see ESI† for details).

Compound 2 is dissolved in THF to obtain a dark purple solution which is cooled to -78 °C and passed into another flask containing black selenium powder (2: Se = 1: 4 molar)ratio). A light green color is obtained after stirring the solution for ten minutes. The green color of the solution is becoming more intense when stirring is continued for twenty minutes. Then the mixture is stirred for 3 h to obtain a brown solution with unreacted selenium powder. Stirring is continued for another 2.5 h to produce a clear orange solution. The volume of the THF solution is reduced to 2 mL under vacuum. Finally, 3 mL of toluene are added and the orange solution is stored at -32 °C in a freezer to form small orange blocks/needles of 3 in 30-32% yield. Compound 3b is comparatively more soluble in THF than 3a. Very recently the synthesis and isolation of (NHC)₂Si₂O₃ and (NHC)₂Si₂O₄ were reported by reacting (NHC)2Si with N2O and O2, respectively.12 The formation of (NHC)₂Si₂O₃ and (NHC)₂Si₂O₄ depends on the source of oxygen. Importantly, when (NHC)₂Si₂O₃ was further reacted with N₂O led to the isolation of decomposed by-products and thus (NHC)₂Si₂O₄ was not obtained. It is well known that NHC mostly favors the formation of coordinate σ-bonds while cAAC forms both coordinate and electron sharing covalent σ-bonds depending on the electronic situation of the involved silicon atom.15

We have carried out the reaction of 2a and Se-powder in 1:2, 1:3, and 1:4 molar ratios. The reaction in a 1:2 molar ratio does not produce the green intermediate color. A dark brown

solution was obtained. The solvent was removed and the dry residue was extracted with n-hexane to obtain a brown filtrate and crystalline 3a in 10–12% yield. The concentrated n-hexane solution was stored at -32 °C in a freezer. No crystals were formed. The removal of solvent (n-hexane) produced an oily material. The reaction in a 1:3 molar ratio proceeds first to a lighter green intermediate color. In the following step a lighter orange solution was obtained from which the crystalline powder of 3a was isolated in 17–20% yield.

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The crystals of 3a-b are stable in air for several days and retain their dark orange color for a week while THF solutions of 3a-b slowly loose their color when exposed to air. Orange powders of 3a-b decompose above 285 °C (3a), 245 °C (3b) to give light yellow solids of cAAC=Se.17 This is concluded from mass spectrometry (see ESI†). Compound 3a was further characterized by EI-MS mass spectrometry (m/z (100%); 944.2) (see ESI†). The UV-vis spectra of compounds 3a-b recorded in THF solution show absorption bands at 422 nm (3a) and 402 nm (3b), respectively (see ESI†) which are close to the values obtained from theoretical TD-DFT calculation (400-440 nm; Tables S10 and S11†). Relative transitions are explained from KS-MO of 3a shown in Fig. S15.† The infrared (IR) spectrum of 3a (measured in the range of 400-4000 cm⁻¹) showed a sharp absorption band at 547 cm⁻¹. It is close to the theoretically calculated values of 533.3 cm⁻¹ ($v_{Si=Se}$) and 355.1 cm⁻¹ (v_{Si-Se}) of 3a. Additionally, 3a is investigated by Raman spectroscopy (see ESI†). Raman spectra are recorded on solid sample of 3a which exhibit Raman bands at 1490.9 cm⁻¹ and 1475.9 cm⁻¹ with a shoulder. A strong Raman band $(\nu_{Si=Si})^{9c}$ was observed at 478 cm⁻¹ for (cAAC)₂Si₂ which is not present in 3a. Both the compounds 3a-b are studied by solution and solid state NMR measurements. 1H and 13C NMR resonances are very broad and hence not much informative (Fig. S11†). ²⁹Si and ⁷⁷Se NMR resonances are not observed. The zwitterionic nature (Schemes 2 and 3) of compound 3 might be the reason for the broadening of the NMR resonances. However, the corresponding chemical shift values of carbene carbon, silicon, and selenium atoms are theoretically calculated and given in the ESI.†

Structural descriptions of 2a-b are given in ESI.† Compound 3a crystallizes in the space group $P2_1/n$ and possesses a center of inversion within the molecule. The asymmetric unit of 3a contains the $(Me_2\text{-cAAC})SiSe_2$ fragment. The complete molecular structure of 3a generated from applying inversion symmetry is shown in Fig. 1.

The Se=Si(μ -Se)₂Si=Se unit (alike C shown in Scheme 1) is coordinated by two Me₂-cAAC ligands. Both silicon atoms adopt a four coordinate distorted tetrahedral geometry. The C_{cAAC}-Si

Scheme 3 Resonance structures of compound 3.

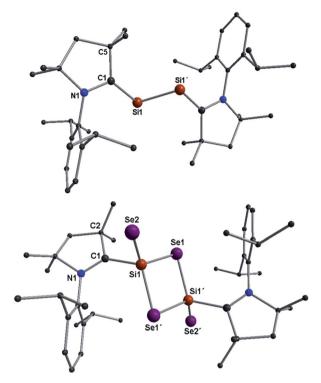


Fig. 1 Molecular structures of compounds 2a (top), 3a (bottom). H atoms are omitted for clarity. Selected experimental [calculated at R-M06-2X/SVP for the singlet state] bond lengths [Å] and angles [°] (as averages of two independent molecules): for 2a/3a; C1-Si1A 1.887(4)/1.931(4) [1.877/1.947], Si1A-Si1A' 2.254(2)/3.056 [2.244/3.083], C1-N1 1.342(5)/1.311(5) [1.343/1.309]; C1-Si1A-Si1A' 103.67(14)/123.94 [102.16/123.51]. For 3a; Si1-Se1 2.2874(10) [2.318], Si1-Se1' 2.3046(10) [2.319], Si1-Se2 2.1510(10) [2.156]; Se1-Si1-Se1' 96.55(4) [96.52], Si1-Se1-Si1' 83.45(4) [83.32], C1-Si1-Se2 97.86(11) [96.58], C1-Si1-Se1 109.85(11) [107.85], C1-Si1-Se1' 113.81(11) [113.33], Se2-Si1-Se1 119.05(4) [121.1], Se2-Si1-Se1' 120.35(4) [121.67].

bond length of 3a is 1.931 (4) Å which is close to that in 1a (1.944 (2) Å)^{15a} but larger than that in 2a (1.887(4) Å) (Table S1†). This suggests that the bond between carbene carbon and silicon is a donor bond ($C_{cAAC} \rightarrow Si$) (Scheme 3), rather than a donoracceptor partial double bond^{9c} in 2a as illustrated in Scheme 2. The Si1-Se1 and Si1-Se2 bond distances of 3a are 2.2874(10)/ 2.3046(10), and 2.1510(10) Å, respectively, suggesting single bond (Si1-Se1, Si1-Se1') and double bond (Si1=Se2) character (Scheme 3).14 The Si1-Se1/Se1' bond distances are close to the values reported for $(SiSe_2)_n$ (A) (2.275 Å). The Se-Si-Se bond angle in Si₂Se₂ four membered ring of 3a is 96.55(4)° which is sharper (by $\sim 3.5^{\circ}$) than that of A (100.0(1)°). This might be due to the coordination of Me₂-cAAC to each silicon atom. The Si₂Se₄ core of compound 3a is structurally similar to that of (NHC)₂Si₂O₄ compound reported by Robinson et al.^{12a} The silicon-silicon bond distance is 3.056 Å in 3a while that of $(NHC)_2Si_2O_4$ is 2.3980(11) Å which is due to the larger size of the selenium atoms.

We have performed DFT calculations to illustrate the electronic structure and bonding scenario of **3a** (refer Computational Details in ESI†). The optimized geometry of **3a** at the M06-2X/SVP level shows a strong resemblance with the X-ray

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crystal structure of 3a (Fig. 1 and S14†). The electronic structure and bonding features of 3a are illustrated using NBO analysis as implemented in Gaussian09. The calculations reveal that C1 is connected to Si1 by a single bond with electron occupancy of 1.94701 e which is primarily located on the C1 (77%) center. The N1-C1 bond in 3a is significantly shorter (1.309 Å) than in 2a (1.343 Å) due to the strong π -bonding interaction to disrupt $C1 \leftarrow Si1$ back donation. This finding also reveals that the C1 is bound to the Si1 as a singlet carbene donor (C1→Si). On the other hand Si1 also binds to Se2 by a single bond and Se contains three lone pairs. But the Si1-Se2 bond length is 2.15 Å which is significantly shorter than the single bond length (2.28 Å and 2.07 Å in H_3Si -SeH and H_2Si =Se, respectively). It is surprising to see that the lone pair occupancies on the Se2 are 1.960, 1.713, and 1.717 e, respectively. The lowering in occupancy of the last two lone pairs can be envisaged as some sort of donor-acceptor type interaction with the Si1 atom, in turn making the bond shorter (Scheme 3).

Topological and topographical analyses are also performed for further illustration of the bonding features in 3a using QTAIM (Quantum Theory of Atoms in Molecules) calculations (see computational details in ESI†).

The electron density, $\rho(r)$, at the (3,-1) bond critical points (BCPs) of C1-Si1 (0.095) and Si1-Se2 (0.104) bonds along with the respective Laplacian $[\nabla^2 \rho(r); +0.240 \text{ and } +0.051]$ indicate closed-shell interaction i.e., donor-acceptor bond (Table S9†). This is further supported by 2D Laplacian plot of (3,-3) critical points (Fig. 2, bottom). The Delocalization Index (DI) value of C1-Si1 (0.43) is lower than for an ordinary C-Si bond in H₃C-SiH₃ (0.55), indicating the presence of weak C1-Si1 donor type bonding. In case of the Si1-Se2 bond the DI value donor (0.6;

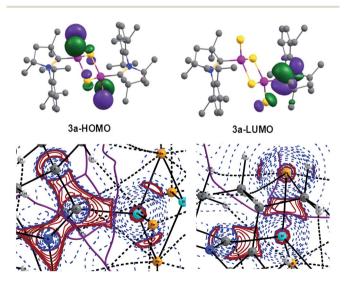


Fig. 2 (Top) Computed KS-MO of 3a at R-M06-2X/TZVP//R-M06-2X/ SVP level. Hydrogen atoms are omitted for clarity. (bottom) Laplacian distribution $[\nabla^2 \rho(r)]$ in N1–C1–Si1 (left) and C1–Si1–Se2 plane (right) of **3a.** Solid lines indicate the areas of charge concentration $(\nabla^2 \rho(r) < 0)$ while dotted lines mean the charge depletion ($\nabla^2 \rho(r) > 0$). The range of contours of the Laplacian is -8×102 to $+8 \times 102$. Solid lines connecting atomic nuclei (black) are the bond paths and those lines (purple) separating the atomic basins indicates the zero-flux surface crossing the molecular plane

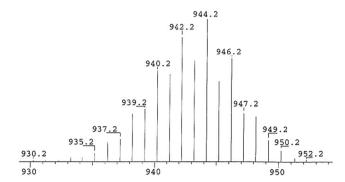


Fig. 3 (a) Experimental EI-mass spectrum of compound 3a

 $Si1 \rightarrow Se2$) is close to that of the Si-Se single bond (0.58) in H₃Si-SeH in accordance with the NBO results discussed above. The real bonding in 3 is a combination of two resonating structures as shown in Scheme 3. In contrast the lower but positive value of Laplacian (+0.051) indicates closed-shell binding nature to lesser extent. We presume that the more electronegative Se is reluctant to share its lone pairs to the adjacent Si center in turn contributing towards equal sharing between the partners.

Conclusions

We have shown that carbene coordinated diatomic silicon(0) species (cAAC)₂Si₂ (2a-b) can react with black selenium powder in a 1:4 molar ratio in THF at -78 °C to rt to produce molecular compound (cAAC)₂Si₂Se₄ (3a-b). Orange powders of 3a-b are stable under an inert atmosphere for nearly a month and decompose above 245 °C. Dark orange crystals of 3a-b retain their colors in air for a week. They are soluble in polar organic solvents, such as THF, while partially soluble in toluene and nhexane. The molecular structure of 3a was confirmed by X-ray single crystal diffraction and EI-mass spectrometry (Fig. 3). A comparison between the bond parameters of 2a and 3a unambiguously led to the conclusion that the Si₂(0) unit in 2a is stabilized by a donor acceptor type bond between 2cAAC and (0) Si=Si(0), while its derivative Si₂Se₄ of 3a has been prevented from undergoing polymerization by strong σ-donation of the cAAC molecules (Schemes 2 and 3). The bonding and stability of 3a have been further studied by theoretical calculations. To the best of our knowledge, this is the first report on a neutral ligandstabilized molecular Si₂Se₄ species. 18,19

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