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A novel and convenient synthesis towards 2-pyridylselenium compounds: X-ray crystal structure of 4,4′-dimethyl-2,2′-dipyridyl diselenide and tris(2-pyridylseleno)methane

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Abstract

Various 2,2′-dipyridyl diselenides were prepared by a simple and convenient method employing non-cryogenic conditions. The diselenide anion, Se_2^{2-} formed by reducing elemental selenium with 100% hydrazine hydrate in sodium hydroxide reacts *in situ* with 2-bromopyridines to afford the title compounds in good to excellent yields. Hydrazine hydrate readily cleaves the selenium-selenium bond in these diselenides to generate 2-pyridylselenolate anion, which reacts with halomethanes to afford 2-pyridylseleno methanes. X-ray crystal structure of 4,4′-dimethyl-2,2′-dipyridyl diselenide (**4**) and tris(2-pyridylseleno)methane (**10**) is described.

Keywords: Diselenide; Pyridyl; Hydrazine; Phase-transfer catalyst

1. Introduction

Symmetrical and unsymmetrical pyridyl selenium compounds have attracted a great deal of attention because of their synthetic utility in organic chemistry [1] and biochemistry [2]. Since they serve as excellent precursors of metal chalcogenolates $M(SeR)_n$ ($M = Li$, Zn, Cd, Hg; $n = 1,2$) for the generation of semiconducting materials [3], a number of methods for their preparation have been developed. The frequently employed methods involve expensive reducing agents [4], require controlled experimental conditions [5,6] and thus are not practical for large scale preparations. Therefore, the development of a practical, efficient and quick process is quite desirable. We herein wish to report a novel and convenient method for the preparation of various 2,2′-dipyridyl diselenide and 2-pyridylseleno methanes in high yields along with the X-ray crystal structure of 4,4′-dimethyl-2,2′-dipyridyl diselenide (**4**) tris(2-pyridylseleno)methane (**10**).

2. Results and discussion

2.1. Preparation of methyl substituted 2,2′-dipyridyl diselenide

Elemental selenium suspended in dimethylformamide reacts with 100% hydrazine hydrate in the presence of NaOH at room temperature to give dark green solution containing diselenide anion [7]. The diselenide anion thus formed reacts *in situ* with the various 2-bromopyridines to afford the title compounds in good to excellent yields (Scheme 1).

In the course of our investigations, it was found that elemental selenium can also be reduced by sodium hydroxide in the presence of a phase transfer catalyst. The subsequent reaction with 2-bromopyridines afford mainly the diselenide along with the corresponding monoselenides (10–20%) indicating that the species chemically equivalent Se_2^{2-} and Se^{2-} are formed (Scheme 2).

2.2. Preparation of 2-pyridylseleno methanes

2,2′-Dipyridyl diselenides can be quantitatively reduced to 2-pyridylselenolate anion using 100% hydra-

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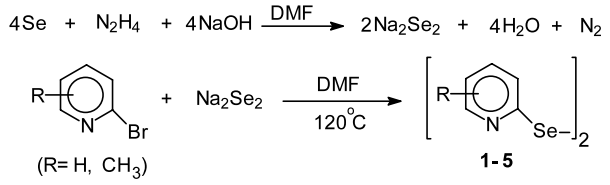
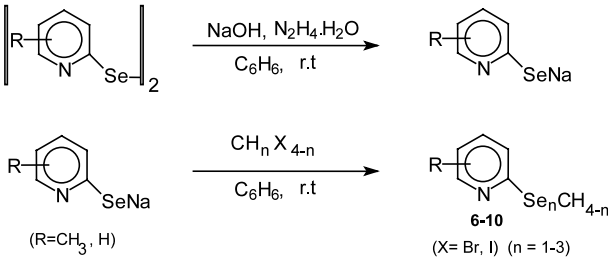


Scheme 1. Preparation of 2,2′-dipyridyl diselenide using hydrazine hydrate (100%).

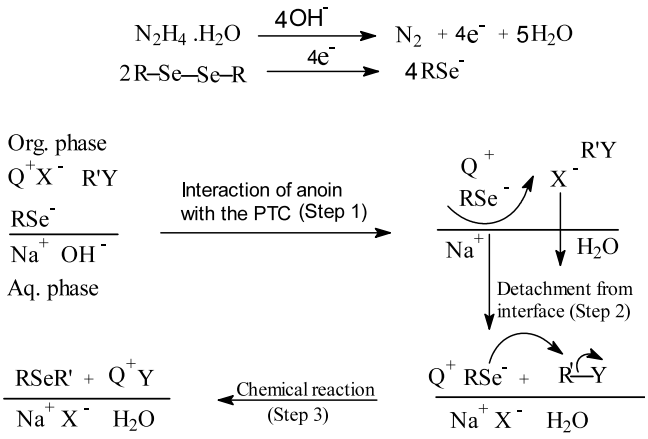
zine hydrate at room temperature in the presence of NaOH in aprotic solvents such as *n*-pentane, *n*-hexane, benzene and THF. The anion thus formed reacts readily with various halomethanes (mono-, di- and trihalomethanes) to give the desired compounds in good to excellent yieids (Scheme 3).

These reactions when carried out in the presence of phase-transfer catalyst viz.; polyethleneglycol-400 and tetrabutylammonium bromide, in an effort to improve the efficiency of the reaction, marginally increases the yields of the reactions. It, therefore, appears that the phase-transfer catalyst may not be involved in the production of the selenolate anion and only catalyzes the substitution reaction with various halomethanes. As part of our studies we also examined the solvent effect on the efficiencies of these reactions employing different solvents. The efficiency of the reaction in various solvents is in the following order: benzene > THF > pentane = hexane. On the basis of our experimental findings, a tentative interfacial mechanism for the above reaction is proposed in Scheme 4.

The reaction of selenolate anion with iodomethane or diiodomethane gave the desired compounds in nearly quantitative yields. In contrast, its reaction with tribromomethane gave both the bis(2-pyridylseleno)methane and tris(2-pyridylseleno)methane in almost equal proportions. 2-Methylseleno picolines are foul smelling liquids whereas the corresponding bis and tris(2-pridylseleno)methanes are pale yellow crystalline solids. All the compounds prepared were characterized by elemental analysis and various spectroscopic techniques viz., ^{1}H-NMR, ^{13}C-NMR, ^{77}Se-NMR, IR and Mass Spectral studies. In the ^{1}H-NMR spectra of tris(2-pyridylseleno)methane the signal corresponding to the hydrogen atom attached to the sp^3 carbon appears in the aromatic region (δ, 7.32 ppm) because of the cumulative electron-withdrawing influence of three pyridylseleno moieties. ^{77}Se (completely decoupled)-NMR spectra of methyl substituted 2,2′-dipyridyldiselenide (**2**, **3** and **5**) were recorded in $CDCl_3$ employing selenic acid as an external



Scheme 3. Preparation of 2-pyridylseleno methanes.



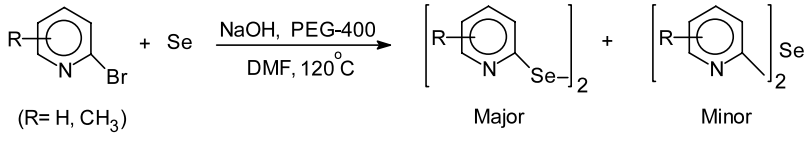
Scheme 4. Interfacial mechanism of the reaction for the preparation of 2-pyridylseleno methanes.

reference. The selenium signal in compound **2**, **3** and **5** appears at −576.7, −584.4 and −594.3 (δ, ppm), respectively. It appears that the methyl group *ortho* to the selenium atom releases more electron density into the pyridine ring, resulting in the reduction of π-interaction between the pyridine ring and the lone pair of electrons on the selenium atom, causing increase in the electron density on the selenium atom in 3,3′-dimethyl-2,2′-dipyridyl diselenide when compared with the corresponding diselenides.

2.3. Solid state structural features of *4* and *10*

In order to understand structural details, single crystal X-ray diffraction study was carried out. A perspective view of structure of **4** and **10** with atom numbering scheme is given in Figs. 1 and 2, respectively, with selected bond lengths and angles in Table 1.

Each pyridine ring in **4** is substituted at 2 position with average Se–C bond length 1.934 (4) Å and at 4 position with average H_3C–C bond length 1.497 (6) Å.



Scheme 2. Preparation of 2,2′-dipyridyl diselenide using PEG-400 and NaOH.

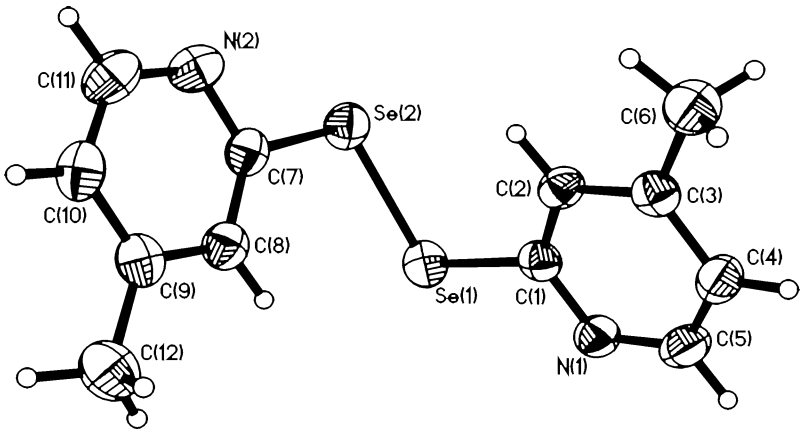


Fig. 1. Perspective view of 4,4′-dimethyl-2,2′-dipyridyl diselenide with atom numbering scheme (40% probability level).

Table 1
Selected bond distances (Å) and angles (°) for compound **4** and **10**

Compound **3**			
Se(1)–C(1)	1.938(4)	Se(1)–Se(1)#1	2.2973(7)
N(1)–C(1)	1.323(6)	N(1)–C(5)	1.344(6)
C(2)–C(3)	1.391(8)	C(3)–C(6)	1.490(6)
C(1)–Se(1)-Se(2)	102.47(12)	C(1)–N(1)–C(5)	115.6(4)
N(1)–C(1)–C(2)	125.0(4)	N(1)–C(1)–Se(1)	110.2(3)
C(2)–C(1)–Se(1)	124.8(3)	C(1)–C(2)–C(3)	118.9(4)
C(4)–C(3)–C(2)	116.7(5)	N(1)–C(5)–C(4)	123.7(4)
Compound **13**			
Se(1)–C(2)	1.918(6)	Se(1)–C(1)	1.939(4)
N(1)–C(2)	1.313(8)	N(1)–C(6)	1.341(8)
C(2)–Se(1)–C(1)	100.3(3)	C(2)–N(1)–C(6)	117.9(6)
Se(1)#1–C(1)–Se(1) #2	108.7(3)	N(1)–C(1)–Se(1)	120.7(4)
N(1)–C(2)–C(3)	123.3(5)	C(3)–C(2)–Se(1)	115.9(4)
C(4)–C(3)–C(2)	118.4(6)	N(1)–C(6)–C(5)	122.9(6)

Symmetry transformations used to generate equivalent atoms for **3**: #1 $-x+1, y, -z+1/2$. Symmetry transformations used to generate equivalent atoms for **13**: #1 $-y+1, x-y+1, z$ # 2 $-x+y, -x+1, z$.

The X–C–Se–Se, torsion angles, X = C or N are 4.3° (4) and −176.5° (3), respectively, which indicate that Se–Se bond lies ca. in the plane of each pyridine ring. The C–Se–Se–C torsion angle for this compound is −89.28° (18) responsible for reduced inter-atomic repulsive interaction between the lone pair of electrons on selenium atoms. The molecular geometry of the pyridine ring is normal in terms of bond lengths and bond angles. Short contacts are observed between Se(2) and H(2) (2.852 Å) and Se(1) and H(8) (2.906 Å), which are significantly shorter than the sum of the van der Waals radii 3.4 Å [8]. It is probably the reason for the Se–Se bond lying close to the plane of the pyridine rings. A unique feature of this structure is the presence of intermolecular non-bonded interactions between the selenium-selenium atoms (Se···Se = 3.878 Å).

In the crystal lattice of tris(2-pyridylseleno)methane, the molecule is located on a three-fold axis with the bonding at the sp^3 carbon regarded as essentially tetrahedral. The geometry of the 2-pyridylseleno moiety in the tris(2-pyridylseleno)methane differs substantially from that in 2,2′-dipyridyl diselenide [3b]. The orientation of the 2-pyridylseleno ring is such that nitrogen atoms are in the *cis*, *cis* position with respect to the Se(1)–C(1) group, whereas they are in the *trans*, *trans* position with respect to the Se–Se group in 2,2′-dipyridyl diselenide. The N–C(2)–Se(1) and C(3)–C(2)–Se(1) bond angles are 120.7° (4) and 115.9° (4),

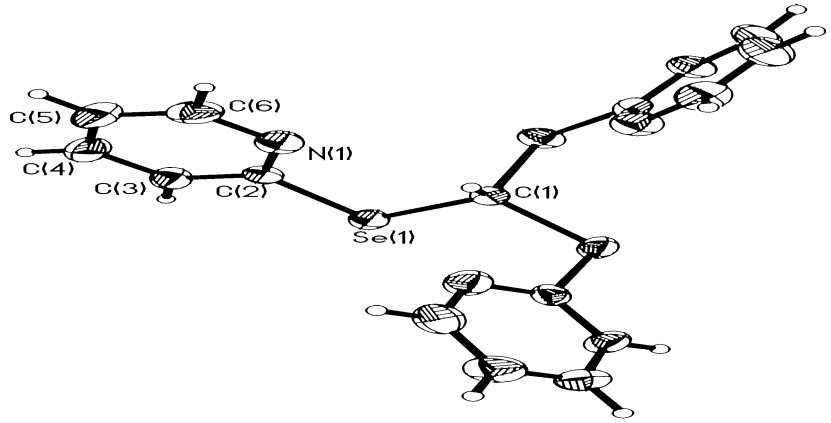


Fig. 2. Perspective view of tris(2-pyridylseleno) methane with atom numbering scheme (40% probability level).

respectively, and lies more towards ideal 120° bond angle, contrary to that observed in 2,2′-dipyridyl diselenide. It is proposed that this be due to the absence of Se···H repulsive interaction in **10**. The angle between the two pyridine ring planes is 76.8° (4). An unusually short Se···Se contact distance 3.152 Å is found between the two molecules and this distance is 0.848 Å shorter than the accepted van der Waals contact distance [8].

3. Experimental

All experiments were carried out in dry oxygen-free nitrogen atmosphere. Infrared spectra were recorded between KBr pellets on a Perkin–Elmer Model 1430 ratio recording spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on Bruker AC-300F, 300 MHz spectrometer. ^{77}Se-BCM NMR spectra of the compounds (**2**, **3** and **5**) were recorded on JNM-AL 400 MHz spectrometer. The mass spectra were obtained on a VG-705 11-250J Mass spectrometer. Carbon, hydrogen and nitrogen were estimated micro analytically on Perkin–Elmer 2400CHN elemental analyzer. 2-Bromopyridines were prepared from the corresponding 2-aminopyridines by employing Craig's method [9].

3.1. General method for the preparation of various methyl substituted 2,2′-dipyridyl diselenide

Method A: To a vigorously stirred mixture of powdered sodium hydroxide (1.5 g, 38 mmol), selenium powder (2.0 g, 25 mmol) and dimethylformamide (100 ml), 100% hydrazine hydrate (1 ml, 25 mmol) was added dropwise at room temperature (r.t.). The mixture was stirred for 2 h. Methyl substituted 2-bromo pyridine (4.2 g, 25 mmol) was added drop-wise to the reaction mixture and refluxed for 3–4 h. After all the 2-bromo pyridine was consumed was consumed as evidenced by TLC, the reaction was stopped and diluted with water. The mixture was extracted with diethyl ether (4 × 100 ml) and the organic layer dried over anhydrous sodium sulphate. Solvent was removed on a rota-evaporator and the residue was purified by column chromatography using silica gel and hexane-ethylacetate as eluent (5:1) to give the pure diselenide.

Method B: To a vigorously stirred mixture of powdered sodium hydroxide (1.5 g, 38 mmol), selenium powder (2.0 g, 25 mmol) and dimethylformamide (100 ml) was added PEG-400 (0.5 ml). The mixture was stirred for 2 h. Methyl substituted 2-bromopyridine (4.2 g, 25 mmol) was added drop-wise to the reaction mixture and refluxed for 3–4 h. After all the 2-bromopyridine was consumed as evidenced by TLC, the reaction was stopped and worked up as described previously.

3.1.1. 2,2′-Dipyridyldiselenide (*1*)

Yield 2.8 g (72%) m.p. 48–50 °C [4]. ^{1}H-NMR: δ, 7.07 (q, 2H, 5.5, 1.7, Hz), 7.53 (m, 2H, 1.9, 5.9, 1.7, 5.9, 2.0 Hz), 7.77 (d, 2H, 8.0 Hz), 8.43 (d, 2H, 5.5 Hz).^{13}C-NMR: δ, 121.1, 123.4, 137.3, 149.4, 154.2. IR (KBr, cm^{-1}): 3060, 2960, 2920, 1565, 1552, 1444, 1105, 1076, 1031, 983, 748, 660. Anal. Calc. for: $C_{10}H_8N_2Se_2$; C, 38.22; H, 2.54; N, 8.91. Found: C, 37.93, H, 2.13; N, 8.45%.

3.1.2. 6,6′-Dimethyl-2,2′-dipyridyldiselenide (*2*)

Yield 2.9 g (68%) m.p. 62–63 °C. ^{1}H-NMR: δ, 2.52 (s, 6H), 6.92 (d, 2H, 7.6 Hz), 7.43 (t, 2H, 7.7 Hz), 7. 61 (d, 2H, 7.8 Hz). ^{13}C-NMR: δ, 24.2, 120.5, 136.0, 137.5, 153.6, 158.5. ^{77}Se-NMR: δ, −576.76. IR (KBr, cm^{-1}): 3060, 2960, 2920, 1580, 1540, 1430, 1120, 1090, 1020, 840, 780, 660, 540. MS (EI): 344 [M (^{80}Se)]$^+$ (27.1); 264 [M–Se]$^+$ (43.3); 183 [M–Se_2H]$^+$ (81); 92 [M–CH_3PySe_2]$^+$ (100). Anal. Calc. for: $C_{12}H_{12}N_2Se_2$; C, 41.86; H, 3.48; N, 8.13. Found: C, 41.08; H, 3.28; N, 8.42%.

3.1.3. 5,5′-Dimethyl-2,2′-dipyridyl diselenide (*3*)

Yield 3.0 g (71%) m.p. 75–77 °C. ^{1}H-NMR: δ, 2.27 (s, 6H), 7.35 (d, 2H, 8.1 Hz), 7. 68 (d, 2H, 8.1 Hz), 8.27 (s, 2H). ^{13}C-NMR: δ, 17.8, 123.3, 130.7, 136.1, 149.8, 150.7. ^{77}Se-NMR: δ, −584.46. IR (KBr, cm^{-1}): 3030, 2983, 2914, 1579, 1559, 1446, 668, 1219, 1081, 1040, 910, 822, 723, 592, 479. ME (EI): 344 [M (^{80}Se)]$^+$ (34.3); 263 [M–SeH]$^+$ (6.2); 183 [M–Se_2H]$^+$ (100); 92 [M–CH_3PySe_2]$^+$ (60.5). Anal. Calc. for: $C_{12}H_{12}N_2Se_2$; C, 41.86; H, 3.48; N, 8.13. Found: C, 41.12; H, 3.35; N, 8.32%.

3.1.4. 4,4′-Dimethyl-2,2′-dipyridyl diselenide (*4*)

Yield 2.8 g (65%) m.p. 96–98 °C. ^{1}H-NMR: δ, 2.20 (s, 6H), 6.89 (d, 2H, 4.1 Hz), 7.62 (s, 2H), 8.31 (d, 2H, 4.9 Hz). ^{13}C-NMR: δ, 21.0, 123.4, 123.9, 148.8, 149.0, 154.0. IR (KBr, cm^{-1}): 3060, 2960, 2920, 1580, 1540, 1460, 1270, 1120, 1080, 840, 700, 500. ME (EI): 344 [M (^{80}Se)]$^+$ (36); 263 [M–SeH]$^+$ (10.1); 183 [M–Se_2H]$^+$ (100); 92 [M–CH_3PySe_2]$^+$ (63). Anal. Calc. for: $C_{12}H_{12}N_2Se_2$; C, 41.86; H, 3.48; N, 8.13. Found: C, 41.72; H, 3.93; N, 8.2%.

3.1.5. 3,3′-Dimethyl-2,2′-dipyridyl diselenide (*5*)

Yield 3.2 g (75%) m.p. 142–144 °C. ^{1}H-NMR: δ, 2.42 (s, 6H), 7.03 (q, 2H, 5.0, 2.5, 4.8 Hz), 7.34 (d, 2H, 7.4 Hz), 8.30 (d, 2H, 5.1 Hz). ^{13}C-NMR: δ, 20.5, 121.7, 133.5, 136.6, 147.7, 153.0. ^{77}Se-NMR: δ, −594.36. IR (KBr, cm^{-1}): 3030, 2960, 2920, 1664, 1570, 1543, 1460, 1277, 1060, 785, 635, 575, 470. ME (EI): 344 [M (^{80}Se)]$^+$ (19.6); 263 [M–SeH]$^+$ (24.4); 183 [M–Se_2H]$^+$ (100); 92 [M–CH_3PySe_2]$^+$ (62.2). Anal. Calc. for: $C_{12}H_{12}N_2Se_2$; C, 41.86; H, 3.48; N, 8.13. Found: C, 41.45; H, 3.62; N, 8.34%.

3.2. General method for the preparation of 2-pyridylseleno methanes

To a vigorously stirred mixture of powdered sodium hydroxide (0.25 g, 62.5 mmol), phase-transfer catalyst (2.5 mmol), 2,2′-dipyridyl diselenide (12 mmol) and aprotic solvent (40 ml), 100% hydrazine hydrate (0.2 ml, 4 mmol) was added drop-wise at r.t. Stirring was continued for additional 30 min. A solution of halomethane in THF was added drop-wise at 0 °C. After completion of the reaction as evidenced by TLC, the reaction was stopped and worked up as described previously.

3.2.1. 2-Methylseleno pyridine (**6**)

Yield 0.29 g (80%). ^{1}H-NMR: δ, 2.31 (s, 3H), 7.04 (m, 1H, 1.7, 5.2, 6.5 Hz), 7.53 (m, 1H, 1.9, 5.9, 1.7, 5.9 Hz), 7.74 (d, 1H, 1.8, 6.5, 7.9 Hz), 8.52 (d, 1H, 5.3 Hz).^{13}C-NMR: δ, 5.3, 120.7, 123.7, 137.9, 148.6, 152.1. IR (Neat, cm^{-1}): 3053, 2955, 2928, 1562, 1435, 1252, 1034, 847, 773, 665, 546. Anal. Calc. for: C_6H_7NSe; C, 41.86; H, 4.06; N, 8.13. Found: C, 41.42; H, 4.47; N, 8.18%.

3.2.2. 2-Methylseleno-6-picoline (**7**)

Yield 0.29 g (80%). ^{1}H-NMR: δ, 2.38 (s, 3H), 2.45 (s, 3H), 6.76 (d, 1H, 7.5 Hz), 7.03 (d, 1H, 7.7 Hz), 7.27 (t, 1H, 7.4, 7.8 Hz). ^{13}C-NMR: δ, 5.1, 23.9, 118.9, 120.7, 135.6, 154.6, 158.3. IR (Neat, cm^{-1}): 3053, 2955, 2928, 1562, 1435, 1252, 1034, 847, 773, 665, 546. MS (EI): 187 [M (^{80}Se)]$^+$(25.0); 173 [M–CH_2]$^+$ (1.6); 107 [M–Se]$^+$ (100); 93 [M–$SeCH_2$]$^+$ (20.6); 77 [M–SeC_2H_6]$^+$ (14.7). Anal. Calc. for: C_7H_9NSe; C, 45.16; H, 4.84; N, 7.53. Found: C, 45.20; H, 4.97; N, 7.45%.

3.2.3. 2-Methylseleno-5-picoline (**8**)

Yield 0.3 g (82%). ^{1}H-NMR: δ, 2.10 (s, 3H), 2.32 (s, 3H), 7.0–7.13 (m, 2H), 8.15 (s, 1H). ^{13}C-NMR: δ, 5.3, 17.6, 123.8, 129.2, 136.5, 150.0, 151.8(g). IR (Neat, cm^{-1}): 3043, 2977, 2928, 1571, 1451, 1083, 830, 616, 539, 467.MS (EI): 187 [M (^{80}Se)]$^+$ (28.3); 173 [M–CH_2]$^+$ (5.6); 107 [M–Se]$^+$ (100); 93 [M–$SeCH_2$]$^+$ (31.3); 77 [M–SeC_2H_6]$^+$ (5.8). Anal. Calc. for: C_7H_9NSe; C, 45.16; H, 4.84; N, 7.53. Found: C, 45.25; H, 4.92; N, 7.37%.

3.2.4. Bis(2-pyridylseleno)methane (**9**)

Yield 2.7 g (70%). m.p. 65 °C; ^{1}H-NMR: δ, 4.84–4.85 (s, 2H), 6.94 (m, 2H, 6.4, 6.0 Hz), 7.28 (d, 2H, 8.1 Hz), 7.36 (m, 2H, 7.5, 7.6, 8.3 Hz), 8.43 (d, 2H, 5.7 Hz). ^{13}C-NMR: δ, 15.93, 120.0, 125.1, 135.6, 150.0, 155.8. MS (EI): 330 [M (^{80}Se)]$^+$ (5.6); 316 [M–CH_2]$^+$ (1.3); 250 [M–Se]$^+$ (5.8); 235 [M–$SeCH_3$]$^+$ (2.0); 170 [M–Se_2]$^+$ (54.8); 158 [M–$Se_2C_6H_6N$]$^+$ (9.9); 156 [M–Se_2CH_2]$^+$ (7.6); 78 [M–$Se_2C_7H_6N$]$^+$(100). IR (Neat, cm^{-1}): 2922, 2291, 1573, 1458, 1377, 1321, 1281, 1153, 1142, 1079, 983, 866, 720, 646, 616, 411. Anal. Calc. for: $C_{11}H_{10}N_2Se_2$; C, 40.24; H, 3.04; N, 8.53. Found: C, 40.54; H, 3.60; N, 8.37%.

3.2.5. Tris(2-pyridylseleno)methane (**10**)

Yield 1.9 g (50%). m.p. 90–91 °C; ^{1}H-NMR: δ, 7.01–7.05 (m, 3H, 5.4,1.9, 5.3 Hz), 7.38 (m, 4H), 7.43–7.49 (m, 3H, 1.7, 5.6, 1.8, 5.8, 2.0 Hz) 8.52 (d, 3H 5.5 Hz). ^{13}C-NMR: δ, 21.1, 120.7, 15.1, 136.2, 150.0, 156.9. IR (Neat, cm^{-1}): 2924, 1568, 1455, 1377, 1274, 1145, 1077 982, 876, 698, 613, 450. Anal. Calc. for: $C_{16}H_{13}N_3Se_3$; C, 39.67; H, 2.68; N, 8.68. Found: C, 39.54; H, 2.72; N, 8.59%.

3.3. Crystal structure determination and refinement

Intensity data were collected on a Siemens P4 Single crystal diffractometer equipped with molybdenum sealed tube ($\lambda = 0.71073$ Å) and highly oriented graphite monochromator using crystal of dimensions $0.34 \times 0.28 \times 0.25$ mm for **10**, mounted in Lindmann glass

Table 2
Crystal data and structure refinement details for compound **4** and **10**

	4	**10**
Empirical formula	$C_{12}H_{12}N_2Se_2$	$C_{16}H_{13}N_3Se_3$
Formula weight	342.16	484.17
Crystal system, space group	Monoclinic, $P2_1/c$	Rhombohydral (Hex. Setting), $R3c$
Unit cell dimensions		
a (Å)	10.555(1)	12.163(1)
b (Å)	13.195(1)	12.163(1)
c (Å)	40.062(3)	40.062(3)
α (°)	90	90
β (°)	94.32(1)	90
γ (°)	120	120
V (Å^3)	1272.3(2)	5132.7(7)
Z, D_{calc} (Mg m^{-3})	4, 1.786	12, 1.880
Absorption coefficient (mm^{-1})	5.786	6.448
$F(000)$	664	2784
Max/min transmission	0.693, 0.454	1.00, 0.810
θ Range for data collection (°)	2.48–23.98	2.138–25.00
Index ranges	$-12 \le h \le 12$, $0 \le k \le 15$, $-10 \le l \le 0$	$0 \le h \le 14$, $-14 \le k \le 0$, $-47 \le l \le 0$
Reflection collected	2134	1885
Independent reflections	1979 [$R_{int} = 0.0205$]	1009 [$R_{int} = 0.0747$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1979/0/148	1009/0/68
Goodness-on-fit on F^2	1.053	0.984
Data to parameter ratio	13.4: 1	14.84:1
Final R indices, 738 reflections, [$I > 2\sigma(I)$]	$R_1 = 0.0340$, $wR_2 = 0.0807$	$R_1 = 0.0426$, $wR_2 = 0.0990$
R indices (all data)	$R_1 = 0.0456$, $wR_2 = 0.0860$	$R_1 = 0.0679$, $wR_2 = 0.1069$
Largest difference peak and hole (e Å^{-3})	0.441 and −0.518	0.976 and −0.467

capillaries at 293(2) K. The cell parameters and their standard deviation crystals of dimensions were obtained by least square to 40 reflections. The $2\theta-\theta$ scan mode was used with variable scan speed ranging from 2.0 to 60.0° min^{-1} in ω. Three reflections were used to monitor the stability and orientation of the crystal and were remeasured after every 97 reflections. All other relevant information about the data collection and the refinement are presented in Table 2.

The crystal structure of **10** was solved by direct method using SHELX-97 [10] and also refined on F^2 using the same one. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the ideal positions with fixed isotropic U values and were riding with their respective non-hydrogen atoms. A weighting scheme of the form $w=1/[\sigma^2(F_o^2)+0.0534P)^2+2.34P]$, $P=[\max(F_o^2,\ 0)+2*F_o^2]/3$ was used. The refinement converged to a final R value of 0.0400, ($wR_2=0.0991$ for 873 reflections) $[I>2\sigma(I)]$.

The data collection procedure, structure solution and refinement for **4** were essentially the same as that for **10**; 40 reflections for accurate cell parameter determination with weighting scheme of the form $w=1/[\sigma^2(F_o^2)+0.0442P)^2+0.94P]$, $P=[\max(F_o^2,\ 0)+2*F_o^2]/3$. Full details are present in Table 2.

4. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 162448 and 162449for compound **4** and **10**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 IE2, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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