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A novel and facile one-pot synthesis of pyridylselenium compounds through selective bromine–magnesium exchange with isopropylmagnesium halide

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One-pot synthesis of various unsymmetrical 2-bromo-5-pyridylselenium compounds has been carried out under non-cryogenic conditions by selective single bromine–magnesium exchange of 2,5-dibromopyridine using isopropylmagnesium chloride. This exchange gives 2-bromo-5-pyridylmagnesium chloride, which upon the insertion of elemental selenium followed by the treatment with alkyl halide gives the title compounds in good yield. This exchange has also been extended towards bromine–magnesium exchange of 2-bromopyridine for the improved synthesis of 2-pyridylselenium compounds. The molecular structure of 2-bromo-5-selenopyridyltribromomethane has been examined by single crystal X-ray diffraction. This compound crystallizes in the monoclinic space group $P2_1/n$. From the molecular structure it was found that intermolecular Br···Br, N···Se and Se···Br interactions control its crystal packing. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; selenium; pyridine; bromine–magnesium exchange

INTRODUCTION

Pyridylselenium compounds, apart from their usefulness in organic synthesis,[1,2] find wide applications in biochemistry.[3–5] Recently, it has been shown that 2,2′-dipyridyldiselenide is a potential immuno-stimulant and inducer of gamma interferon and other cytokines in human peripheral blood leukocytes.[4] It has also been suggested that organoselenium compounds containing Se–N non-bonded interaction exhibit strong GP_x antioxidant activity.[5] However, the major breakthrough in this field came with the observation that 5-ethyl-6-pyridylthio/seleno acyclouracils are active against HIV-1.[3–5]

Pyridylselenium compounds serve as important ligands that contain a set of nitrogen/selenium donor atoms and, therefore, can provide insight into the competitive coordination behavior between hard and soft Lewis bases towards the same metal center.[6–12] It is also conceivable that complexes of this type with platinum (or even other metal) centers could be used as cytostatic drugs[7] and as a single-source precursor for metal organic chemical vapour deposition.[13–15]

In view of all these applications, efforts have been directed to evolving convenient methodologies for their synthesis.[16,17] All these methodologies describe the synthesis of 2-pyridylselenium compounds. No reports have so far been found discussing the synthesis of 2-bromo-5-pyridylselenium compounds. In this paper, we are proposing a practical and scalable one-pot selective synthesis of the title compounds.

Preparation of pyridylselenium compounds have been carried out by metathetical reaction of halopyridine with alkali-metal selenide (generated *in situ* by the reaction of elemental selenium with sodium borohydride) at elevated temperature.[16] Another methodology generally employed involves the reaction of elemental selenium with lithiopyridines.[18] Owing to the instability of the lithiated pyridine the reaction has to be carried out under cryogenic conditions in order to avoid its decomposition. The corresponding pyridylmagnesium halides are comparatively stable even at relatively high temperatures (>25 °C). However, pyridylmagnesium halides are extremely difficult to generate directly from the corresponding halides and magnesium.[19] Meunier and coworkes[20] carried out a halogen–magnesium exchange reaction in 1974 to generate pyridylmagnesium halide.

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Recently, it was successfully quenched with several electrophiles.[19] We applied this exchange on various bromopyridines, which upon selenium insertion, followed by alkylation, give corresponding unsymmetrical pyridylselenium compounds.

RESULTS AND DISCUSSION

Regioselective synthesis of 2-bromo-5-pyridylseleno methanes

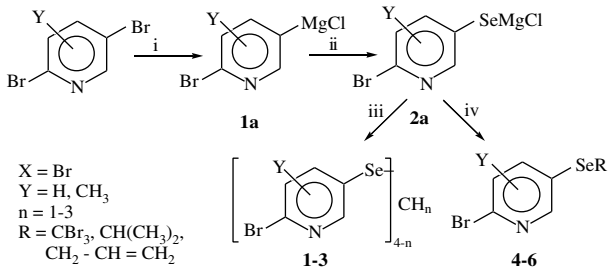
2,5-Dibromopyridine undergoes selective mono bromine–magnesium exchange with isopropylmagnesium chloride in tetrahydrofuran (THF) to give a wine-red solution of 2-bromo-5-pyridylmagnesium chloride (**1a**). This species, upon selenium insertion, gives 2-bromo-5-pyridylselenomagnesium chloride (**2a**), which upon quenching with halomethanes/alkanes gives the corresponding 2-bromo-5-selenopyridyl methanes/alkanes in good yields (Scheme 1).

Pyridylselenomethanes and phenylselenomethanes have traditionally been prepared by the reductive cleavage of the Se–Se bond of diselenide using hydrazine hydrate as a reducing agent.[21,22] This reductive cleavage gives the pyridyl/phenyl selenoate anion, which upon reaction with CBr_4 gives tris(2-pyridylseleno)methane and small quantities of bis(2-pyridylseleno)methane according to Equations (1) and (2). In this reaction, owing to the strong alkaline conditions the bromine in CBr_4 is replaced either by pyridylselenoate or by hydrogen.

$$PySe{-}SePy \xrightarrow[NaOH]{N_2H_4\cdot H_2O,\ THF} PySeNa + N_2 + H_2O \quad (1)$$

$$PySeNa + CBr_4 \xrightarrow[THF]{NaOH} (PySe)_3CH + (PySe)_2CH_2 \quad (2)$$

We found that 2-bromo-5-pyridylselenomagnesium chloride (**2a**) upon reaction with CBr_4 affords 2-bromo-5-selenopyridyltribromomethane along with the small quantity (15%) of 2,2-dibromo-5,5-dipyridyldiselenide as a by-product instead of tris(2-bromo-5-selenopyridyl)methane. Tris (2-bromo-5-selenopyridyl)methane was thus obtained by the reaction of bromoform with 2-bromo-5-pyridylselenomagnesium chloride (**2a**). Our attempt to synthesize bis(2-bromo-5-selenopyridyl)dibromomethane by reacting **2a** with 0.5 equivalents of CBr_4 was unsuccessful, which could be attributed to the prevailing steric hindrance in the compounds. For the preparation of bis(2-bromo-5-selenopyridyl)methane the reaction was carried out using various dihalomethanes.



Reagents and Conditions : i) iPrMgCl, r.t; ii) Se,0°C; iii) $CHnX_{4-n}$; iv) RX

Scheme 1. Preparation of 2-bromo-5-selenopyridylmethanes/alkanes.

Preparation of unsymmetrical substituted 2,2′-dipyridyldiselenides

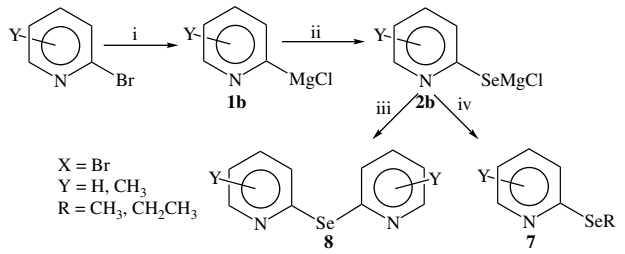
Various methyl-substituted 2-bromopyridines undergo bromine–magnesium exchange upon reaction with an equimolar quantity of isopropylmagnesium chloride to give a wine-red solution containing species **1b**, as shown in Scheme 2. This species is fairly stable at room temperature under nitrogen for a long time. *In situ* addition of elemental selenium to this species changes the color of the solution to yellow due to the presence of species **2b**. When all selenium has dissolved, equimolar quantities of alkylhalide or bromopyridine are added to obtain alkylpyridylselenide or dipyridylselenide respectively, in excellent yields at room temperature. This reaction of bromine–magnesium exchange is sensitive to high temperature and moisture. As the temperature exceeds room temperature the yield of these compounds reduces drastically due to the formation of coupled products

Interestingly, in contrast to the diselenides, which are yellow crystalline in nature, all 2-bromo-5-selenopyridylmethanes are colorless crystals.

All the compounds prepared were analyzed and characterized by elemental analysis and various spectroscopic techniques, viz. ^{1}H NMR, ^{13}C NMR, ^{77}Se NMR, IR and mass spectroscopy and X-ray fluorescence studies.

^{1}H NMR studies

In the ^{1}H NMR spectrum of 2-bromo-5-selenopyridyltribromomethane the signal of the protons ortho to the ring nitrogen appears at δ 8.79 compared with that for 2-bromo-5,5-dipyridyldiselenide at δ 8.53. This is due to a cumulative electron-withdrawing influence of the $SeCBr_3$ group at the



Reagents and Conditions: i) iPrMgCl, r.t ; ii) Se, 0°C; iii) Y-PyBr; iv) RX

Scheme 2. Preparation of unsymmetrical 2-pyridylselenium compounds.

position ortho to this proton and the bromo substituents on the ring. A careful study of chemical shift values of the ^{77}Se resonance reveals that selenium shielding increases in the order $BrPySeCH_3$ > $(BrPySe)_2CH_2$ > $(BrPySe)_3CH$ > $BrPySeCBr_3$. From this observation it appears that the substituent attached to selenium affects the polarizability of the electron cloud of the relatively soft selenium atom. In 2-bromo-5-selenopyridylmethanes, a deshielding of the ^{77}Se resonance is observed each time a hydrogen of the parent compound $CH_3SePyBr$ is replaced by an SePyBr group: $BrPySeCH_3$ (270 ppm), $(BrPySe)_2CH_2$ (333 ppm), $(BrPySe)_3CH$ (460 ppm). Interestingly, maximum deshielding is observed when all the hydrogen atoms of methane are replaced by bromine, as in $BrPySeCBr_3$. This may be attributed to the fact that the more polarizable bromine atom can more effectively polarize the electron density at the selenium atom, thus causing deshielding in the ^{77}Se resonance.

X-ray fluorescence

For the elemental analysis of all the compound prepared, the 59.54 keV γ-rays from the ^{241}Am (300 mCi) radioisotopes were used to excite the characteristic X-rays of the elements present in the sample, which were recorded using an Si(Li) detector. A typical spectrum of 2-bromo-5-selenopyridyltribromomethane with 59.54 keV photon energy is shown in Fig. 1. The elements present in 2-bromo-5-selenopyridyltribromomethane are recognized by their peak energy.

X-ray crystallography

In the course of our investigation, an attempt was made to grow single crystals of the title compounds to allow unambiguous structure determination. Single crystals of 2-bromo-5-selenopyridyltribromomethane were grown by dissolving the compound in dichloromethane and then layering it with hexane. A perspective view of the structure **4** with the atom numbering scheme is given in Fig. 2 and selected geometric parameters are listed in Table 1.

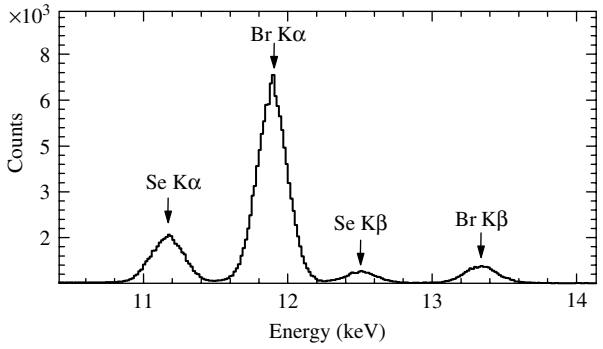


Figure 1. Typical excitation spectrum of the 2-bromo-5-selenopyridyltribromomethane.

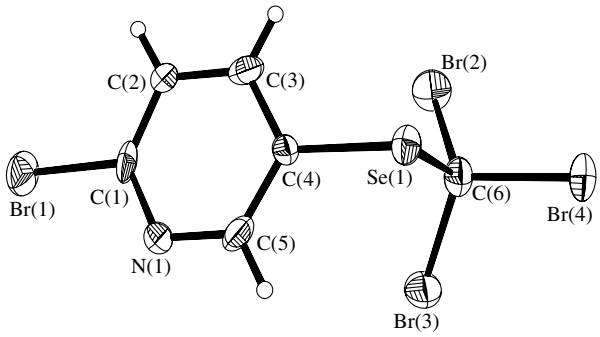


Figure 2. Perspective view of structure of 2-bromo-5-selenopyridyltribromomethane.

Table 1. Bond lengths (Å) and bond angles (°) for (2-bromo-5-selenopyridyl)tribromomethane

Se1–C4	1.912(9)	Se1–C6	1.959(10)
Br1–C1	1.901(9)	Br2–C6	1.938(10)
Br3–C6	1.931(11)	Br4–C6	1.940(10)
C1–C2	1.375(15)	C2–C3	1.400(15)
C3–C4	1.391(14)	C4–C5	1.382(14)
N1–C1	1.305(13)	N1–C5	1.338(13)
Br3–C6–Br4	110.2(5)	Br2–C6–Br3	108.8(5)
Br2–C6–Br4	109.9(5)	Se1–C6–Br2	111.5(5)
Se1–C6–Br4	103.7(5)	Br3–C6–Se1	112.6(5)
C5–C4–Se1	120.7(8)	C3–C4–Se1	120.8(7)

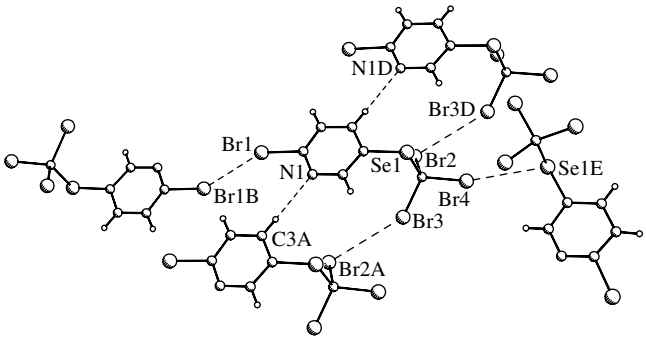


Figure 3. Br–Br secondary interaction in 2-bromo-5-selenopyridyltribromomethane.

This compound crystallizes in the space group $P2_1/n$. The greatest deviation from ideal tetrahedral geometry for C6 is manifested in the Br(3)–C(6)–Se(1) and Br(4)–C(6)–Se(1) bond angles of 112.6° and 103.7° respectively. The C–Br bond distance in this compound deviates from the C–Br in CBr_4 (1.912(39) Å). The C–Se bond lengths in **4** fall within the normal range of 1.91–1.97 Å.[23–25] The steric strain in this compound is due to the interaction of bulky pyridylseleno moiety with Br(2) and Br(3). The crystal structure clearly demonstrates that the principal

Table 2. The secondary interactions in 2-bromo-5-selenopyridyltribromomethane

	Atoms	Interatomic distance	Symmetry transformation
Br1	Br1	3.569	$(1-x, -y, 1-z)$
Br2	Br3	3.780	$(x, 1+y, z)$
Br4	Br1	3.584	$(2.5-x, 0.5+y, 0.5-z)$
Br1	Se1	3.786	$2-x, 1-y, 1-z$
Br4	Se1	3.584	$2.5-x, 0.5+y, 0.5-z$
H3A	N1	2.506	$(x, 1+y, z)$
C–H···N	angle	173.2°	

means for relieving the congestion in this compound is by lengthening of the C(6)–Se(1) bond and enlargement of the C(4)–Se(1)–C(6)–Br(4) dihedral angle. The most interesting feature in **4** is the existence of a variety of short contacts, making this molecule a good example of a structure containing supramolecular Br···Br and Se···Br close contacts.[26] The association between molecules via Br···Br, Br···Se and C–H···N interactions is shown in Fig. 3 and the geometric parameters associated with these interactions are collected in Table 2.

EXPERIMENTAL

All the experiments were carried out in a dry, oxygen-free nitrogen atmosphere. IR spectra were recorded in KBr pellets on a Perkin–Elmer Model-1430 ratio recording spectrometer. ^{1}H and ^{13}C, NMR spectra were recorded in $CDCl_3$ using tetramethylsilane as an internal standard on a Joel-300 MHz spectrometer. ^{77}Se spectra was recorded using dimethylselenide as an external reference. The mass spectra were obtained on a VG-70 511-250J mass spectrometer. Carbon, hydrogen and nitrogen were estimated microanalytically using a Perkin Elmer 2400 CHN elemental analyzer. 2,5-Dibromopyridine was prepared from aminopyridine by first employing *N*-bromosuccinimide[27] then further bromination was carried out using Craig's method.[28]

General method for the preparation of 2-bromo-5-pyridylseleno methanes

To a vigorously stirred solution of i-PrMgCl (20 mmol) in 20 ml of THF was added 2,5-dibromopyridine at room temperature. Stirring was continued for 2 h and then elemental selenium was added slowly under an ice bath. After an additional 1 h stirring, a solution of halomethane in THF was added slowly under an ice bath. The reaction mixture was allowed to stir for an additional 2 h until the thin-layer chromatography (TLC) spot corresponding to diselenide completely disappeared. The reaction was then worked up as given before. The purification on silica column required different polarities.

2-Bromo-5-selenopyridyl methane was collected using 1% ethyl acetate in hexane. 2-Bromo-5-selenopyridyl propene was collected using 3% ethyl acetate in hexane. Bis(2-bromo-5-selenopyridyl)methane, tris(2-bromo-5-selenopyridyl)methane and 2-bromo-5-selenopyridyl tribromethane were collected using 10% ethyl acetate in hexane.

*2-Bromo-5-selenopyridylmethane (**1**)*

Yield 1.5 g (60%). ^{1}H NMR: δ, 2.31 (s, 3H, CH_3), 7.29 (d, 8 Hz, 2H, meta to N), 7.43 (q, 2 Hz and 8 Hz, 2H, para to N), 8.53 (d, 2 Hz, 2H, ortho to N). ^{13}C NMR: δ, 150.77, 146.04, 139.81, 127.9, 7.45. ^{77}Se NMR: δ 270. MS (EI): 251 $[CH_2SePyBr]^+$; (16.6); 236 $[SePyBr]^+$ (89.3); 156 $[PyBr]^+[PySe]^+$ (76.3); 78 [Br, PySe] (100). IR (neat, cm^{-1}): 3053, 3055, 2955, 2928, 1562, 1435, 1252, 1034, 847, 773, 665, 546. Elemental analysis Anal. Found: C, 28.64; H, 2.36; N, 11.13. Calc. for C_6H_6BrNSe: C, 28.68; H, 2.39; N, 11.15%.

*Bis(2-bromo-5-seleno pyridyl)methane (**2**)*

Yield 2.88 g (60%), m.p. 180 °C. ^{1}H NMR: δ, 4.15 (s, 2H, flanked by selenium satellites), 7.42 (d, 8.1 Hz, 2H, meta to N), 7.68 (dd, 2 Hz and 8 Hz, 2H, para to N), 8.47 (d, 2 Hz, 2H, ortho to N). ^{13}C NMR: δ, 153.86, 143.47, 122.19, 128.70, 125.97, 21.92. ^{77}Se NMR: δ, 333. MS: 486 $[M]^+$ (21.3), 250 $[CH_2SePyBr]^+$ (100), 236 $[HSePyBr]^+$ (704), 170 $[CH_2PySe]^+$ (49.7), 156 $[PySeH]^+$ (10.2). IR (KBr, cm^{-1}): 2924, 1654, 1543, 1463, 1377, 1351, 1097, 1077, 1004, 825, 787, 720, 627, 483. Anal. Found: C, 27.13; H, 1.629; N, 5.73. Calc. for $C_{11}H_8Br_2N_2Se_2$: C, 27.04; H, 1.639; N, 5.73%.

*Tris(2-bromo-5-seleno pyridyl)methane (**3**)*

Yield 2.88 g (60%), m.p. 165 °C. ^{1}H NMR: δ, 7.32 (s, 1H), 7.43 (d, 8.1 Hz, 3H, meta to N), 7.66 (dd, 2 Hz and 8 Hz, 3H, para to N), 8.49 (d, 2 Hz, 3H, ortho to N). ^{13}C NMR: δ, 25.3, 122.20, 125.97, 128.35, 142.53, 154.23. ^{77}Se NMR: δ, 460. Anal. Found: C, 27.01; H, 1.41; N, 5.73. Calc. for $C_{16}H_{10}Br_3N_3Se_3$: C, 26.64; H, 1.40; N, 5.78%. Elemental analysis (XRF): Se, 33.23; Br, 33.82.

*2-Bromo-5-selenopyridyltribromomethane (**4**)*

Yield 6.0 g (62%), m.p. 140 °C. ^{1}H NMR: δ, 7.62 (d, 8 Hz, 2H, meta to N), 8.07 (dd, 2 Hz and 8 Hz, 2H, para to N), 8.76 (d, 2 Hz, 2H, ortho to N). ^{13}C NMR: δ, 156.49, 146.10, 145.51, 130, 129, 1.795. ^{77}Se NMR: 552. MS (EI): 487 $[M]^+$ (8.9); 407 $[Br_3CPyBr]^+$ (100); 329 $[Br_2CPyBr]^+$ (12.9); 249 $[BrCHPyBr]^+$ (37.6); 236 $[PyBrSeH]^+$ (7.6); 156 $[PySeH]$ (107). IR (KBr, cm^{-1}): 3855, 3752, 3651, 2925, 2854, 1654, 1541, 1459, 1440, 1377, 1352, 1092, 1072, 1004, 838, 787, 739, 677, 666, 644, 493.

*3-(2-Bromo-5-selenopyridyl)-1-propene (**5**)*

Yield, 3.3 g (60%), m.p. 60 °C. ^{1}H NMR: δ, 3.62 (d, 12 Hz, 2H, CH_2), 5.02 (d, 13.5 Hz, 1H, CH_2 cis), 5.2 (d, 14.5, 1H CH_2), 6.05 (m, 7.35, 12.0 13.5, 14.5 Hz, 1H, CH), 7.18 (d, 8 Hz, 2H, meta to N), 7.52 (dd, 2 Hz and 8 Hz, 2H, para to N), 8.46 (d, 2 Hz, 2H,

ortho to N). ^{13}C NMR: δ, 150.77, 149.3, 146.04, 139.81, 127.9, 120.5, 116.7, 56.8. ^{77}Se NMR: δ, 297.

*2-(2-Bromo-5-selenopyridyl)-2-methylethane (**6**)*

Yield 3.34 g (60%), viscous oil. ^{1}H NMR: δ, 1.35 (d, 6H, $2CH_3$), 3.10 (m, 1H, CH), 7.15 (d, 8 Hz, 2H, meta to N), 7.56 (dd, 2 Hz and 8 Hz, 2H, para to N), 8.47 (d, 2 Hz, 2H, ortho to N). ^{13}C NMR: 154.4, 149.1, 147.0, 137.5, 126.4, 5.8, 1.7. ^{77}Se NMR: δ, 395.

General method for the preparation of unsymmetrical alkylpyridylselenide/ dipyridylselenide

2-Bromopyridine (20 mmol) in THF (20 ml) was treated with i-PrMgCl (20 mmol) at room temperature. After 2 h of stirring, 20 mmol of elemental selenium was added in parts. When all the selenium had dissolved, an equivalent amount of alkylhalide/bromopyridine was added under an ice bath. The reaction was monitored using TLC; when the spot corresponding to diselenide disappeared the reaction mixture was washed with distilled water and extracted with dichloromethane. The product was purified by column chromatography using 1% ethyl acetate in hexane.

*2-Methylselenopyridine (**7**)*

Yield 3.0 g (80%), oil. ^{1}H NMR: δ, 2.31 (s, 3H, CH_3), 7.04 (m, 1H, 1.7, 5.2, 6.5 Hz, meta to N), 7.53 (m, 1H, 1.9, 5.9, 1.7, 5.9 Hz ortho to Se), 7.74 (d, 1H, 1.8, 6.5, 7.9 Hz, para to N), 8.52 (d, 1H, 5.3 Hz, ortho to N). ^{13}C NMR: δ, 5.3, 120.7, 123.7, 137.9, 148.6, 152.1. ^{77}Se NMR: δ, 245.0 IR (neat, cm^{-1}): 3053, 2955,

Table 3. Crystal data and structure refinement for 2-bromo-5-selenopyridyltribromomethane

Empirical formula	$C_6H_3Br_4NSe$
Formula weight	487.69
Temperature (K)	293(2)
Diffractometer	Siemens P4
Radiation used, wavelength (Å)	Mo Kα, 0.71073
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	
a (Å)	10.370(1)
b (Å)	6.202(1)
c (Å)	17.260(2)
α (°)	$\alpha = 90$
β (°)	$\beta = 91.18(1)$
γ (°)	$\gamma = 90°$
Volume (Å^3)	1109.8(2)
Z, calculated density (Mg m^{-3})	4, 2.919
Absorption coefficient (mm^{-1})	17.733
F(000)	880
Crystal size (mm^3)	0.23 × 0.18 × 0.14
Max. and min. transmission	0.886, 0.338
θ range for data collection (°)	2.27 to 24.00
Scan type	$2\theta-\theta$
Scan speed (° min^{-1})	Variable, 2.0 to 60.0 in ω
Scan range (ω)	1.0° plus Kα separation
Background measurement	Stationary crystal and stationary counter at the beginning and end of scan, each for 25.0% of total scan time
Index ranges	$-11 \le h \le 0$, $-7 \le k \le 0$, $-19 \le l \le 19$
Reflections collected	1844
Independent reflections	1717 ($R_{int} = 0.0735$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1717/0/110
Goodness-of-fit on F^2	1.015
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.1066P)^2 + 0.18P]$, $P = (\max(F_o^2, 0) + 2F_c^2)/3$
Data to parameter ratio	15.6 : 1
Final R indices, 1345 reflections [$I > 2\sigma(I)$]	$R_1 = 0.0566$, $wR_2 = 0.1403$
R indices (all data)	$R_1 = 0.0751$, $wR_2 = 0.1483$
Extinction coefficient	0.0021(6)
Largest diff. peak and hole (e$^-$ Å^{-3})	1.432 and −1.486

2928, 1562, 1435, 1252, 1034, 847, 773, 665, 546. Anal. Found: C, 41.42; H, 4.47; N, 8.18. Calc. for C_6H_7NSe: C, 41.86; H, 4.06; N, 8.13%.

6,6′-Dimethyl-2,2′-dipyridylselenide (8)

Yield 2.5 g (50%). ^{1}H NMR: δ, 2.52 (s, 6H, CH_3), 6.92 (d, 7.6 Hz, 2H, meta to N), 7.43 (t, 7.7 Hz, 2H, para to N), 7.61 (d, 7.8 Hz, 2H, ortho to Se). ^{13}C NMR: δ, 24.2, 121.5, 137.0, 138.5, 153.6, 158.5. ^{77}Se NMR: δ, 405. IR (KBr, cm^{-1}): 3060, 2960, 2920, 1580, 1540, 1430, 1120, 1070, 1020, 840, 780, 660. MS (EI): 264 [M $-^{80}$ Se]$^+$ (24.3); 188 $[CH_3PySeH]^+$ (6.0); 92 $[CH_3PyH]^+$ (100). Anal. Found: C, 52.53; H, 4.20; N, 10.20. Calc. for $C_{12}H_{12}N_2Se$; C, 54.54; H, 4.54; N, 10.60%.

Crystal structure determination and refinement

Intensity data were collected on a Siemens P4 single crystal diffractometer equipped with a molybdenum-sealed tube ($\lambda = 0.710\,73$ Å) and highly oriented graphite monochromator using a crystal of dimensions $0.23 \times 0.18 \times 0.14$ mm^3 for compound **5**, mounted in Lindemann glass capillaries at 293(2) K. The crystal structure was solved by direct methods and refined on F^2 using SHELX-97.[29] $C_6H_3Br_4NSe$, $M = 487.69$, monoclinic, $P2_1/n$, $a = 10.370(1)$, $b = 6.202(1)$, $c = 17.260(2)$ Å, $\beta = 91.18(1)^\circ$, $V = 1109(2)$ Å^3, $Z = 4$, 1717 unique data ($\theta_{max} = 24.0^\circ$), $R = 0.0056$ (1345[$I \geq 2\sigma(I)$) reflections), $\omega R = 0.148$ (all data), $\rho_{max} = 1.43$ e$^-$ Å^{-3} (located in between the Se1 (0.991 Å) and C4 (1.515 Å) of the aromatic moiety and is deviated 0.620 Å from the least-squares plane of the pyridine ring). The cell parameters and the standard deviation of the crystal dimensions were obtained by least squares to 40 reflections. The $2\theta-\theta$ scan mode was used with variable scan speed ranging from 2.0 to 60° min^{-1} in ω. All the other relevant information about the data collection and the refinement are presented in Table 3. All non-hydrogen atoms were refined anisotripically. Correct positions for nitrogen and carbon in the crystal structure of **4** were established from refinement of alternative positions and subsequent comparison of the R values. CCDC deposition number 218 109.

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