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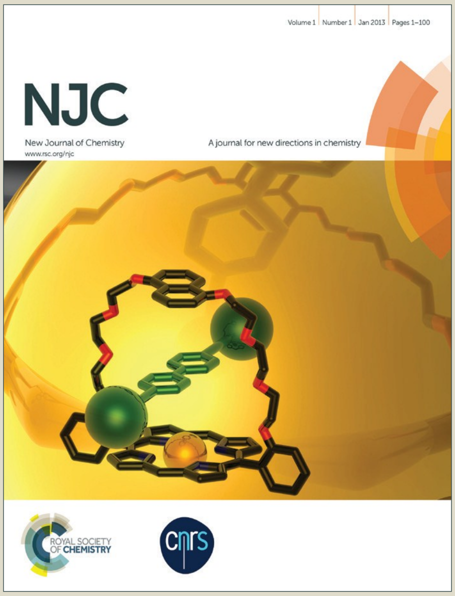

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ARTICLE

Metal complexes with bis(2-pyridyl)diselenoethers: Structural chemistry and catalysis

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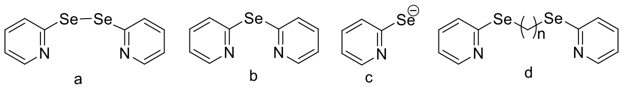
Bis(2-pyridyl)diselenoethers with the general formula $(2\text{-PySe})_2(CH_2)_n$ [n = 1, 3 and 4] react with CuI, $AgNO_3$, $CuCl_2{\cdot}2H_2O$ and $CoCl_2{\cdot}6H_2O$ under formation of products with molecular or multidimensional structures depending on the stoichiometry of the reactants and the conditions applied. The versatility of this class of selenium-containing ligands is demonstrated with the synthesis and structural characterization six new complexes of the compositions $[CuCl_2\{(2\text{-PySe})_2CH_2\}]_n$ (**1**), $[Cu_4I_4\{(2\text{-PySe})_2CH_2\}_2]$ (**2**), $[CuCl_2\{(2\text{-PySe})_2(CH_2)_3\}_2]$ (**3**), $[CoCl_2\{(2\text{-PySe})_2(CH_2)_3\}]_n$ (**4**), $[Ag\{(2\text{-PySe})_2\text{–}(CH_2)\}_3]_n(NO_3)_n$ (**5**) and $[CuCl_2\{(2\text{-PySe})_2(CH_2)_4\}]_n$ (**6**), respectively. The Cu(I) complex (**2**) was tested as catalyst in cross-coupling reactions.

Introduction

In recent years, pyridylselenium derivatives like $(2\text{-Py})_2Se$, $(2\text{-PySe})_2$ and $[2\text{-PySe}]^-$ (Scheme 1, examples a-c) containing both hard (nitrogen) and soft (selenium) donors have been employed as ligands to build mono-, bi- and polynuclear coordination compounds and a series of materials with interesting magnetic and catalytic properties.[1-11] The synthesis of new materials needs a rational control about the structural design of the compounds. Particularly for the synthesis of oligomeric and polymeric compounds, an exact control of spacers between the functional groups is required in order to get knowledge about the positions and structural arrangements of the subjects of investigation of the new materials. Although the chemistry of 2-pyridylchalcogen derivatives is well documented,[1-11] the synthesis of complexes containing bis(2-pyridyl)diselenoether (Scheme 1, structures d) as ligands remained widely unexplored.



Scheme 1. Examples of pyridylselenium derivatives.

The only information about crystal structures of this class of compounds are private communications of a few examples involving Ag(I) and Zn(II) centers registered by Jones and coworkers and almost no chemical information is given.[12-15] The complexes $[Ag\{(2\text{-PySe})_2CH_2\}_2\{N(SO_2CH_3)_2\}_2]$, $[Ag\{(2\text{-PySe})_2CH_2\}_2\{N(SO_2)_2(C_6H_4)\}_2]$ and $[Ag\{(2\text{-PySe})_2CH_2\}_2\{(N\text{-}(SO_2)_2(BrC_6H_4)_2\}_2]$ contain $(2\text{-PySe})_2CH_2$ chelated to Ag^+.[12-14] In $[ZnCl_2\{(2\text{-PySe})_2CH_2\}]$, the same ligand coordinates with its nitrogen atoms twice to Zn^{2+}.[15]

Coordination compounds containing cobalt,[16] palladium,[17] nickel[18] or copper ions[19] are frequently used as catalysts for coupling and functionalization reactions. This is an important process for the preparation of many materials of biological, chemical and pharmaceutical interest.[20,21] Copper becomes more and more attractive because of its redox properties and low costs compared with the other cited elements.[22] The used ligands should make the copper ions soluble in organic solvents.[23] Three main classes of bidentate ligands with nitrogen and/or oxygen donor atoms are already explored. Complexes with 1,10-phenantroline or 2,2-bipyridine ligands attracted most attention.[24] On the other hand, the development of sustainable methodologies using recycled sources are under constant development, mainly by the necessity to replace solvents obtained by fossil sources in industrial processes.[25] In such processes, also glycerol, a side-product of biofuel production, was recently proposed as a valuable “green solvent”.[26] The availability of glycerol on a large scale and at low costs, combined with its intrinsic properties as non-flammable and non-toxic solvent makes it an ideal solvent for the development of more sustainable syntheses.[27]

In this paper, we present the synthesis and characterization of a series of bis(2-pyridyl)diselenoethers with the general formula $\{(2\text{-PySe})_2(CH_2)_n\}$ (n = 1, 3 and 4) and the syntheses of six new complexes thereof: $[CuCl_2\{(2\text{-PySe})_2CH_2\}]_n$ (**1**), $[Cu_4I_4\{(2\text{-PySe})_2CH_2\}_2]$ (**2**), $[CuCl_2\{(2\text{-PySe})_2(CH_2)_3\}_2]$ (**3**),

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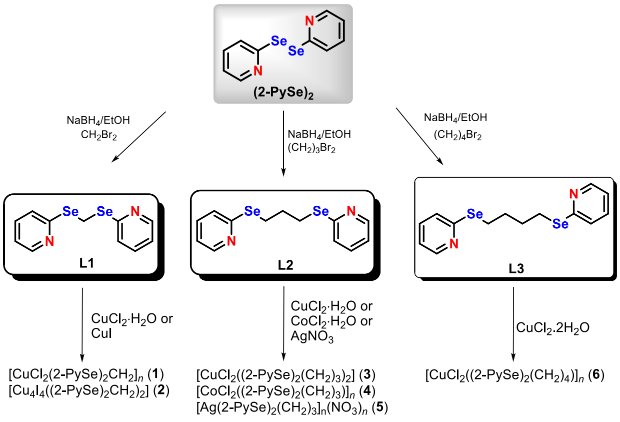
$[CoCl_2\{(2\text{-}PySe)_2(CH_2)_3\}]_n$ (**4**), $[Ag\{(2\text{-}PySe)_2(CH_2)_3\}]_n(NO_3)_n$ (**5**) and $[CuCl_2\{(2\text{-}PySe)_2(CH_2)_4\}]_n$ (**6**). We also describe preliminary results of the use of **2** as catalyst in cross-coupling reactions using glycerol as solvent.

Results and discussion

Synthesis and structural characterization

Based on our previous results about the use of 2-pyridylselenide ligands in coordination chemistry,[28] we started this work with the synthesis of three bis(2-pyridyl)diselenoethers of the general formula $\{(2\text{-}PySe)_2(CH_2)_n\}$ with n = 1 (**L1**), 3 (**L2**) and 4 (**L3**) by a reaction of bis(2-pyridyl)diselenide and sodium borohydride followed by the addition of the corresponding dibromoalkane. The compounds were purified by flash chromatography in all cases and isolated as a colorless powder (**L1**), a yellow oil (**L2**) and a yellow powder (**L3**). The signals of the methylene groups appear in the ^1H NMR spectra of the selenoethers between 1 and 5 ppm and 6 and 8 ppm, respectively. The ratios between the signals of aromatic and alliphatic protons support the structure and purity of the novel compounds.

The bis(2-pyridyl)diselenoethers **L1** to **L3** were used for complex formation reactions with metal ions of different hardness (Cu^+, Ag^+, Cu^{2+} and Co^{2+}) . Scheme 2 summarizes the performed reactions and their products.



Scheme 2. Synthesis of the bis(2-pyridyl)diselenoethers **L1, L2** and **L3** and their reactions with metal ions.

The obtained products **1** - **6** were structurally characterized by X-ray diffraction and their structures are shown in the Figures 1-6. Ellipsoid representations of all compounds are given as Figures S1 to S6 of the Supplementary Material together with selected bond lengths and angles.

Green crystals of compound **1** are obtained by the reaction of **L1** and one equivalent of $CuCl_2\cdot 2H_2O$. ESI+ mass spectra of the compound show intense peaks at m/z = 392.8480 for the molecular ion corresponding to $[C_{11}H_{10}CuN_2Se_2]^+$ (calc. 392.8470). In this compound, the copper atoms exist in dimeric $\{Cu_2Cl_4\}$ units connected by two chlorine atoms. The copper atoms possess a square-pyramidal environment formed by three chlorine and two nitrogen atoms from the ligands **L1**. The ligands **L1** connect the dimeric $\{Cu_2Cl_4\}$ units through the nitrogen atoms under formation of a three-dimensional polymeric structure as is presented in Fig. 1.

Yellow crystals of compound **2** were prepared in a very similar way as used for the synthesis of **1**, but with Cu(I) iodide instead of Cu(II) chloride. The structure of **2** shows a core with four copper atoms being connected by two μ_3-iodine atoms. Surrounding the core, four nitrogen and two selenium atoms from the ligands **L1** and two more iodine atoms complete the tetrahedral coordination environment of the core. Each two copper ions present an alternate coordination environment by the exchange of an iodine by a nitrogen atom. The observed copper-copper distances Cu1···Cu2#1 and Cu2···Cu1#1 of 2.8481(3) Å can be interpreted as a week interactions.

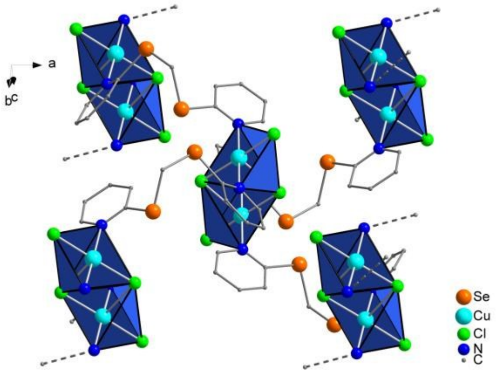


Fig. 1. Representation of the polymeric structure of **1**. For clarity, the hydrogen atoms are not shown.

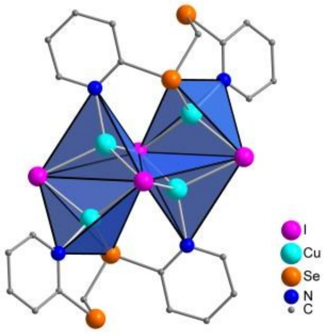


Fig. 2. Projection of the molecular structure of the compound **2**. For clarity, the hydrogen atoms are not shown.

Green crystals of the molecular compound **3** were obtained by the reaction between two equivalents of **L2** and one equivalent of $CuCl_2\cdot 2H_2O$ in THF. The ligand/copper ratio of 2:1 drives to the formation of a molecular compound and prevents from the building of a polymeric structure like in compounds **1** or **6**. The molecular structure is supported by the ESI+ mass spectrum of the compound showing an intensive peak at m/z = 871.7509 for the molecular ion corresponding to $[C_{26}H_{28}Cl_2CuN_4Se_4 + Na]^+$ (calc. 871.7540). The copper ion is coordinated in a highly distorted octahedral coordination geometry formed by two nitrogen and two selenium atoms of two different ligand molecules and two chlorine atoms, where each pairs of similar atoms are located in *trans* positions.

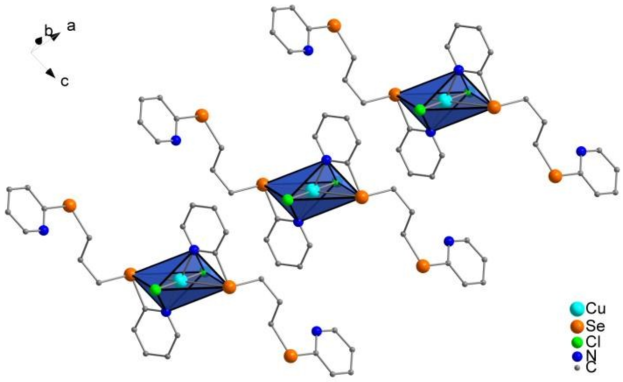


Fig. 3. Representation of the molecular structure of the compound **3**. For clarity, the hydrogen atoms are not shown.

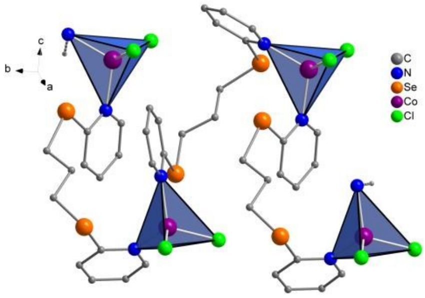


Fig. 4. Representation of the polymeric structure of the compound **4**. For clarity, the hydrogen atoms are not shown.

Blue crystals of compound **4** were obtained from the reaction of equivalent amounts of **L2** and CoCl$_2$·6H$_2$O upon stirring the mixture for 7 hours at room temperature and subsequent slow evaporation. The ESI+ mass spectrum of the compound shows an intense peak at m/z = 451.8499, which can be assigned to an ion of the composition [CoN$_2$Se$_2$C$_{13}$H$_{14}$Cl]$^+$ (calc. 451.8508). In the crystal structure of **4**, the Co atoms adopt a tetrahedral geometry formed by two nitrogen atoms from different ligands and two chlorine atoms. The ligands **L2** connect the CoCl$_2$ units and build a polymeric zigzag chain along the crystallographic *b* axis.

The polymeric compound [Ag{(2-PySe)$_2$(CH$_2$)$_3$}]$_\infty$(NO$_3$)]$_\infty$ (**5**) was isolated in crystalline form from the reaction of **L2** with one equivalent amount of AgNO$_3$ in EtOH. Figure 5 shows the two-dimensional polymeric structure formed by the [Ag{(2-PySe)$_2$(CH$_2$)$_3$}]$^+$ units without the NO$_3^-$ anions. In the infrared spectra the nitrate counter ion presents an asymmetric (N=O) stretch at 1640 cm^{-1} and symmetric (N=O) stretch at 1336 cm^{-1}. ESI+ mass spectra show an intense peak at m/z = 464.8544, which is assigned to the mononuclear unit [AgSe$_2$C$_{13}$H$_{14}$N$_2$]$^+$ (calc. 464.8538), showing that the polymeric arrangements are broken in the gas phase. The bi-dimensional polymeric structure of **5** is built by the coordination of the N and Se atoms of **L2** to different Ag atoms. In this compound we observe a coordination of the Se atoms to the Ag$^+$ ions, which are commonly regarded as a 'medium soft' acceptor.

Compound **6** was obtained as green crystals by the reaction of **L3** and one equivalent amount of CuCl$_2$·2H$_2$O in a THF/MeOH mixture. ESI+ mass spectra of the compound show intense peaks at m/z = 434.8949 for the corresponding monomeric [CuSe$_2$C$_{14}$H$_{16}$N$_2$]$^+$ unit (calc. 434.8940). Each copper atom adopts an octahedral geometry formed by two N and two Se atoms from two different ligands and two chlorido ligands. The ligand **L3** follows the same chelating mode of complexation as found in the compounds **2** and **3**. The one-dimensional polymeric chains grow along the crystallographic *a* axis.

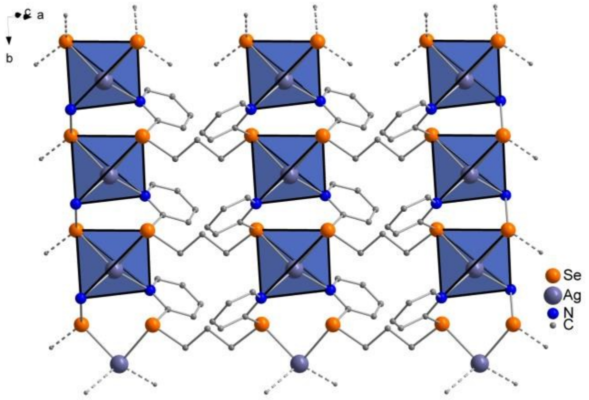


Fig. 5. Representation of the polymeric structure of [Ag{(2-PySe)$_2$(CH$_2$)$_3$}]$^+$ (**5**). Hydrogen atoms and NO$_3^-$ ions have been omitted for clarity.

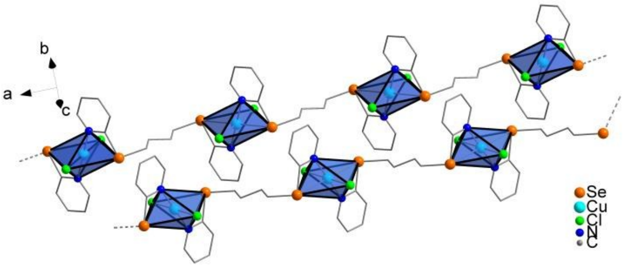
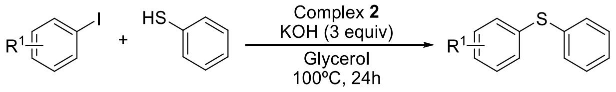


Fig. 6. Projection of the polymeric structure of the compound **6**. For clarity, the hydrogen atoms are not shown.

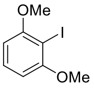
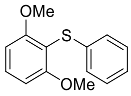
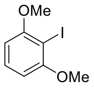
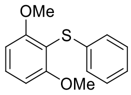
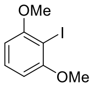
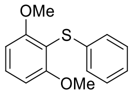
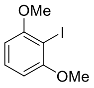
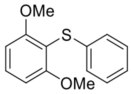
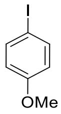
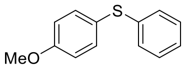
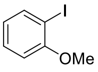
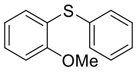
*Catalytic activity of compound **2***

To exemplify the use of the new class of compounds described in the present article as potential catalysts, we tested compound **2** for well-established C–S coupling reactions.[20e, 20g-h] The C–S coupling was studied in accordance with the reactions presented in Table 1. A mixture of ArI (1 mmol), thiophenol (1.5 mmol), KOH (3 mmol) and various amounts of **2** were dissolved in 10 mL glycerol and kept at 100ºC for 24 h. The amount of **2** was varied (2, 3, 4 and 10 mol%) following the data presented in Table 1. We observed that with an increasing amount of the catalyst the yield of the reaction was clearly improved (Table 1: entries 1-4). The use of 10 mol % of **2** gives a yield of 94%. Additionally, we tested the latter conditions for reactions with 4-iodoanisole (entry 5) and 2-iodoanisole (entry 6) and obtained yields of 73% and 94%, respectively. We studied the re-use of the Cu(I)-complex catalyst (**2**) in the glycerol-mediated reaction of **7a** with **8**. We observed, however, that the catalyst was inactive after the first reaction and a black powder was obtained as result of the decomposition of the catalyst. Scheme 3 suggests a mechanism for Cu-catalyzed C–S coupling reactions of aryl iodides and thiols.[20e]

Table 1. C-S coupling reactions of aryl iodide and thiophenol catalyzed by **2** in glycerol as solvent.[a]

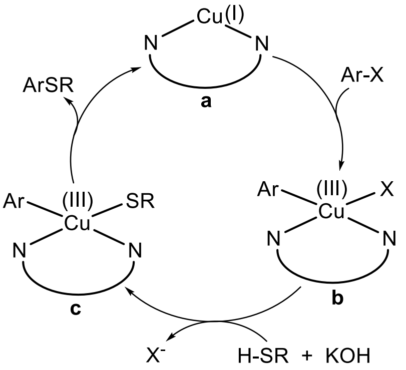


7a-7c **8** **9a-9c**

Entry	Aryl iodide **7**	Mol %	Product **9**	Yield (%)[b]
1	 **7a**	2	 **9a**	63
2	 **7a**	3	 **9a**	78
3	 **7a**	4	 **9a**	82
4	 **7a**	10	 **9a**	94
5	 **7b**	10	 **9b**	73
6	 **7c**	10	 **9c**	94

[a] Reaction conditions: Aryl iodide **7** (1.0 mmol), thiophenol **8** (1.5 mmol), KOH (3.0 mmol), complex **2**, glycerol (10 mL), 100ºC, Argon. [b] Isolated yield after column chromatography.

The mechanism suggests an oxidative addition of the copper atom to the aryl halide molecule under formation of **b**. This first step is followed by the reaction with the thiol compound giving **c**. Reductive elimination of the intermediate **c** can generate the desired sulfide and regenerate the catalyst. The literature suggests that the ligands coordinated to the copper center are acting in the addition of the Cu(I) atom to Ar–X and also stabilize the Cu(III) species as suggested in Scheme 3.



Scheme 3. Proposed catalytic cycle.[20e]

Conclusions

The novel selenoethers **L1**, **L2** and **L3** were synthesized in good yields by reactions of bis(2-pyridyl)diselenide with the corresponding dibromoalkanes. The bis(2-pyridyl)diselenoethers react with different metal precursors under formation of a series of coordination compounds (**1** - **6**). The structural variety of the products shows the great versatility of the ligands containing hard N and soft Se atoms. A preliminary study for the use of compound **2** as catalyst for C–S coupling reactions reflects a high catalytic activity, when compared with literature values.[20e, 20g-h] Studies for acquiring a greater potential of the new bis(2-pyridyl)diselenides and their metal compounds for applications in organic and inorganic synthesis are under development.

Experimental

Preparations and tools

All syntheses were conducted under an Ar atmosphere. The compound bis(2-pyridyl)diselenide was prepared according to procedures reported in the literature.[29] All other analytical grade reagents and solvents were obtained commercially (Aldrich or Vetec), and the solvents were freshly distilled prior to use.[30]

FTIR spectra were recorded on a BRUKER FTIR model Tensor 27 spectrophotometer over the range 4000–400 cm^{-1}. Elemental analyses (CHN) were determined using a VARIO EL (Elementar Analysensysteme GmbH). Melting points were determined on a Microquímica MQAPF-301 melting point apparatus. NMR spectra were obtained on a Bruker DPX-400 NMR spectrometer. Spectra were recorded in $CDCl_3$ solutions. Coupling constants (J) are reported in Hertz. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quintet), m (multiplet). Mass spectra (MS) were measured on a Shimadzu GCMS-QP2010 mass spectrometer and ESI mass spectra were measured with an Agilent 6210 ESI-TOF (Agilent Technologies).

X-Ray diffraction: A Bruker CCD X8 APEX II diffractometer was used for the X-ray structure analyses. The equipment was operated using a graphite monochromator with Mo-Kα radiation (λ = 0.71073 Å). The structures were solved with SHELXS using direct methods.[31] The structures were refined using a full-matrix least squares on F^2 using all data (SHELX crystal structure solution software).[31] All non-hydrogen atoms were refined using anisotropic displacement parameters in SHELXL.[31] The hydrogen atom positions were calculated starting from the idealized positions. The free refinement of hydrogen atom parameters gave a low data/parameter ratio and led to high correlations. Representation of the structures of **1** - **6** (Figures 1 - 6) were designed with DIAMOND.[32] Details about the structure determination are provided in the Electronic Supplementary Information.

*Synthesis of the ligands **L1**, **L2** and **L3***: To a stirred solution of bis(2-pyridyl)diselenide[29] (1 mmol) in EtOH (10 mL) under argon atmosphere was added sodium borohydride ($NaBH_4$) (3 mmol). A light yellow solution was formed. To this solution was added the appropriate dibromoalkane (1 mmol) (**L1**: 1,2-dibromomethane; **L2**: 1,3-dibromopropane; **L3**: 1,4-dibromobutane). The resulting solution was stirred for 8 h at room temperature. After this time, the mixture was diluted with ethyl acetate (20 mL) and washed with water (3x10 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexane/ethyl acetate as eluent.

Properties of bis(2-pyridylseleno)methane (**L1**): colorless crystalline solid. Yield: 81%. Mp: 69-70ºC. $C_{11}H_{10}N_2Se_2$ (328.13 gmol^{-1}): calcd C 40.26, H 3.07, N 8.54; found C 40.22, H 2.99, N 8.48. IR (KBr, cm^{-1}): 3045 (w), 2992 (w), 1601 (s), 1573 (s), 1553 (s), 1458 (s), 1408 (s), 1078 (m), 1038(m), 750 (s), 696 (m), 463 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 8.38 (d, J = 3.19 Hz, 2H), 7.33 (t, J = 6.11 Hz, 2H), 7.21 (d, J = 7.94 Hz, 2H), 6.92 (t, J = 5.01, 2H), 4.78 (s, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 155.50, 149.87, 135.90, 125.08, 120.62, 15.82.

Properties of bis(2-pyridylseleno)propane (**L2**): yellow oil. Yield: 70%. $C_{13}H_{14}N_2Se_2$ (356.18 gmol^{-1}): calcd C 43.84, H 3.96, N 7.86; found C 43.99, H 4.08, N 7,89. IR (KBr, cm^{-1}): 3040 (m), 2987 (m), 2932 (m), 2848 (m), 1601 (s), 1572 (s), 1449 (s), 1411 (s), 1083 (s), 1041(m), 750 (s), 698 (m), 467 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 8.39 (d, J = 4.9 Hz, 2H), 7.40- 7.35 (m, 2H), 7.27 (d, J = 7.9 Hz, 2H), 6.98-6.95 (m, 2H), 3.27 (t, J = 7.2 Hz, 4H), 2.25 (quint, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 155.11, 150.05, 135.88, 125.38, 120.23, 30.93, 25.56.

Properties of bis(2-pyridylseleno)butane (**L3**): yellow solid. Yield: 87%. Mp: 46-47ºC. $C_{14}H_{16}N_2Se_2$ (370.21 gmol^{-1}): calcd C 45.42, H 4.36, N 7.57; found C 45.38, H 4.41, N 7.46. IR (KBr, cm^{-1}): 3036 (w), 2980 (w), 2934 (m), 2861 (w), 1601(w), 1573 (s), 1556 (s), 1452 (s), 1410 (s), 1078 (s), 1044 (m), 757 (s), 698 (m), 471 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 8.38 (d, J = 3.91 Hz, 2H), 7.37-7.33 (m, 2H), 7.25 (d, J = 7.82 Hz, 2H), 6.95-6.92 (m, 2H), 3.18 (t, J = 6.84 Hz, 4H), 1.92 (quint, J = 6.84 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 155.64, 150.01, 135.72, 125.51, 120.33, 30.28, 25.50.

$[CuCl_2\{(2\text{-}PySe)_2CH_2\}]_n$ (**1**): A solution of **L1** (0.050 g, 0.15 mmol) in 4 mL of THF was overlayered with a solution of $CuCl_2{\cdot}2H_2O$ (0.026 g, 0.15 mmol) in 5 mL of MeOH. Slow diffusion of these solutions gave green crystals of **1**. Yield: 85%. *Properties*: Mp: 148 - 149ºC. Elemental analysis: calc. for $CuSe_2Cl_2C_{11}H_{10}N_2$: C 28.56, H 2.18, N 6.06; found C 28.61, H 2.11, N 5.89. IR (KBr, cm^{-1}): 3086 (w), 3005 (w), 2940 (w), 1585 (s), 1558(s), 1480 (s), 1416 (s), 1096 (m), 1053 (m), 782 (s), 472 (w). ESI+MS (m/z): 392.8480 $[CuSe_2N_2C_{11}H_{10}]^+$.

$[Cu_4I_4\{(2\text{-}PySe)_2CH_2\}_2]$ (**2**): CuI (0.057 g, 0.30 mmol) was added to a solution of **L1** (0.050 g, 0.15 mmol) in 15 mL of THF. The mixture was kept at 50ºC for 7 hours. The light yellow precipitate obtained was filtered off and dried under vacuum. Yellow crystals were obtained from the mother solution. Yield: 74%. *Properties*: Mp: 188 - 189ºC. Elemental analysis: calc. for $Cu_4I_4N_4Se_4C_{22}H_{20}$: C 18.63, H 1.42, N 3.95; found C 18.31, H 1.39, N 3.69. IR (KBr, cm^{-1}): 3083 (w), 3057 (w), 2991 (w), 2929 (w), 1611 (s), 1579 (m), 1461 (s), 1417 (s),1089 (m), 1051 (w), 782 (m), 472 (w).

$[CuCl_2\{(2\text{-}PySe)_2(CH_2)_3\}_2]$ (**3**): $CuCl_2{\cdot}2H_2O$ (0.034 g, 0.20 mmol) was added to a solution of **L2** (0.142 g, 0.40 mmol) in 10 mL THF. A green solid immediately starts to precipitate. The mixture was stirred for 3 h at room temperature. The green precipitate was filtered off and crystallized from a mixture of DMF/$CHCl_3$ (1:1). Yield: 41%. *Properties*: Mp: 151 - 152ºC. Elemental analysis: calc. for $CuN_4Se_4C_{26}H_{28}Cl_2$: C 36.88, H 3.33, N 6.62; found C 35.61, H 3.32, N 6.36. IR (KBr, cm^{-1}): 3086 (w), 3053 (w); 2976 (w), 2927 (w); 1585 (s), 1557(s), 1454 (s), 1418 (s), 1087 (m), 1051 (m), 762 (s). ESI+MS (m/z): 871.7509 $[CuN_4Se_4C_{26}H_{28}Cl_2+Na]^+$.

$[CoCl_2\{(2\text{-}PySe)_2(CH_2)_3\}]_n$ (**4**): $CoCl_2{\cdot}\,6H_2O$ (0.095 g, 0.40 mmol) was added to a solution of **L2** (0.142 g, 0.40 mmol) in 15 mL THF. The mixture was stirred for 7 h at room temperature. The blue precipitate obtained was filtered off and dried under vacuum. Blue crystals were obtained from the mother solution. Yield: 32%. *Properties*: Mp: 223 - 224ºC. Elemental analysis: calc. for $CoN_2Se_2C_{13}H_{14}Cl_2$: C 32.13, H 2.90, N 5.76; found C 31.56, H 2.65, N 5.64. IR (KBr, cm^{-1}): 3095 (w), 3074 (w), 2973 (w), 2933 (w), 1588 (m); 1457 (s), 1411 (s), 1089 (m), 1054 (m), 767 (s). ESI+MS (m/z): 451.8499 $[CoN_2Se_2C_{13}H_{14}Cl]^+$.

$[Ag\{(2\text{-}PySe)_2(CH_2)_3\}]_n\,(NO_3)_n$ (**5**): $AgNO_3$ (0.068 g, 0.40 mmol) was added to **L2** (0.142 g, 0.40 mmol) in 10 mL EtOH. The mixture was stirred for 5 h at room temperature. The gray precipitate was filtered off and crystallized from a mixture of DMSO/$CHCl_3$ (1:1). Colorless crystals, yield: 58%. *Properties*: Mp: 91 - 92ºC. Elemental analysis: calc. for $AgN_3O_3Se_2C_{13}H_{14}$: C 29.68, H 2.68, N 7.99; found C 27.82, H 2.68, N 7.48. IR (KBr, cm^{-1}): 3092 (w), 3062 (w), 2943 (w), 1640 (w), 1578 (m), 1560 (m), 1452 (m), 1420 (m), 1336 (s), 1084 (m), 1046 (w), 760 (s). ESI+MS (m/z): 464.8544 $[AgSe_2C_{13}H_{14}N_2]^+$.

$[CuCl_2((2\text{-}PySe)_2(CH_2)_4)]_n$ (**6**): A solution of L3 (0.050 g, 0.1350 mmol) in 4 mL THF was overlayered with a solution of $CuCl_2{\cdot}\,2H_2O$ (0.023 g,0.1350 mmol) in 5 mL MeOH. Slow diffusion of these solutions gave green crystals of **6**. Yield: 95%. *Properties*: Mp: 170 - 171^{O}C. Elemental analysis: calc. for $C_{14}H_{16}Cl_2CuN_2Se_2$: C 33.32, H 3.20, N 5.55; found C 33.15, H 3.08, N 5.29. IR (KBr, cm^{-1}): 3064 (w), 2957 (w), 2923 (m), 2860 (w), 1586 (s), 1455 (s), 1418 (s), 1087 (m), 1051 (m), 772 (s), 481 (w). ESI+MS (m/z): 434.8949 $[CuSe_2C_{14}H_{16}N_2]^+$.

*General procedure for the synthesis and analytical data of **9a**-**9c***: The respective aryl iodide (1.0 mmol), compound **2** (142 mg, 0.1 mmol, 10 mol%), KOH (168 mg, 3 mmol), thiophenol (0.15 mL, 1.5 mmol) and glycerol (10 mL) were added into an argon-filled flask. The contents were then stirred at 100 °C for 24 h. The mixture was cooled to room temperature, diluted with ethyl acetate (20 mL) and washed with saturated NaCl solution (3 x 20 mL). The organic layer was separated, dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using hexane /ethyl acetate.

*Properties of 2,6-dimethoxyphenyl-phenyl-sulfide (**9a**): 2,6-dimethoxyphenyl-phenyl-sulfide* (**9a**): Colorless solid. Yield: 95%. Mp: 91 - 92ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 7.26 (t, J = 8.19 Hz, 1H), 7.07-6.94 (m, 5H), 6.54 (d, J = 8.31 Hz, 2H), 3.7 (s, 6H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ (ppm): 160.72, 137.24, 130.39, 127.62, 125.61, 123.94, 107.03, 103.68, 55.31. MS (relative intensity) m/z: 247 (16), 246 (100), 216 (15), 200 (23), 198 (23), 171 (13), 107 (11), 91 (24), 77 (7), 51 (8).

Properties of 4-methoxyphenyl-phenyl-sulfide (**9b**): Colorless oil. Yield: 87%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 7.32 (d, J = 8.80 Hz, 2H), 7.15-7.01 (m, 5H), 6.79 (d, J = 8.92 Hz, 2H), 3.71 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ (ppm): 159.83, 138.59, 135.27, 128.97, 128.32, 125.76, 124.44, 115.04, 55.25. MS (relative intensity) m/z: 218 (6), 217 (15), 216 (100), 200 (55), 129 (17), 77 (13).

Properties of 2-methoxyphenyl-phenyl-sulfide (**9c**): Colorless oil. Yield: 79%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 6.45 (dd, J^1 = 8.55 Hz, J^2 = 1.58 Hz, 2H), 6.41-6.30 (m, 4H), 6.21 (dd, J^1 = 7.68 Hz, J^2 = 1.66 Hz, 1H), 6.00-5.94 (m, 2H), 2.94 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ (ppm): 157.36, 134.79, 131.82, 131.44, 129.17, 128.50, 127.06, 124.18, 121.32, 111.02, 55.86. MS (relative intensity) m/z: 217 (14), 216 (100), 200 (18), 182 (12), 168 (16), 129 (13), 91 (11), 77 (11).

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Notes and references

† Electronic Supplementary Information (ESI) available: Crystallographic parameters and details of data collection and refinement are presented in Table S1; graphical representation of ORTEP views of compounds **1**-**6** are presented in Figures S1- S6. ^{1}H-NMR, ^{13}C-NMR, FT-IR and ESI+ MS spectra described in the experimental part are also presented in Figures S7-S37. See DOI: 10.1039/x0xx00000x.

‡ CCDC 1403721-1403726 contain the supplementary crystallographic data for **1**-**6**. 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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