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Synthesis and structural chemistry of Co^{II}, Cu^{II}, Cu^{I} and Pd^{II} complexes containing a flexible monoselenoether ligand†

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Monoselenoether ligand [$PySeCH_2Py$] (L) reacts with $CoCl_2$, $CuCl_2$, CuI and $Pd(OAc)_2$ resulting in the formation of molecular or polymeric complexes. The synthesis and structural elucidation of the complexes [$CoCl_2(L)$] (1), [$Cu_2Cl_4(L)_2$] (2a), [$CuCl_2(L)$] (2b), [$Cu_2Cl_2(PySe)_2$] (2c), [$Cu(2\text{-}PyCOO)_2$] (2d), [$Cu_2I_2(L)_2$] (3), [$Cu_2I_2(L)$]$_n$ (4) and [$Pd_2(CH_3COO)_2(PySeCHPy)_2$]$\cdot 7H_2O$ (5) demonstrate the versatility of this class of pyridylselenium ligands. For all compounds, the ligand offers N and/or Se atoms as donors and, in the case of 5, the ligand also builds C–Pd bonds to generate a cyclometallated palladium(II) complex.

Organoselenium compounds are being studied extensively due to their numerous applications in organic transformations,[1] pharmacological properties,[1,2] catalytic activity,[3] semiconducting materials[4] and coordination chemistry.[5] Pyridylselenium derivatives are a special family of ligands which have soft selenium and intermediate nitrogen donor atoms and may participate in a variety of coordination modes.[5] Some 2-pyridylselenium ligands are presented in Fig. 1, and the species **a–c** have been employed to build mono-, bi- and polynuclear coordination compounds.[1,3b,5] Our group, in 2015, described the use of bis(2-pyridyl)diselenoethers (Fig. 1, structure **c**) as versatile ligands for copper-catalyzed C–S bond formation in glycerol.[3a]

Although the chemistry of 2-pyridylselenium derivatives (Fig. 1, structures **a–c**) is well-known,[3,5] the synthesis of complexes containing 2-picolyl selenopyridine (Fig. 1, structure **d**) as a ligand remains widely unexplored. To our knowledge, there are only two articles describing the synthesis of 2-picolyl selenopyridine (**d**)[1,6] and no information on the crystal structures of this class of compounds was found.

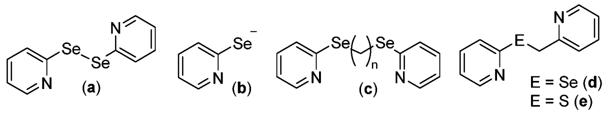

Fig. 1 Examples of 2-pyridylselenium compounds.

On the other hand, the syntheses of compounds containing a monothioether ligand as represented in structure **e** (Fig. 1) are well described.[3c,e,7] The monothioether **e** is considered a flexible ligand in coordination chemistry.[3c,7a,b] Prakash and co-workers[3e] reported the synthesis and structure of half sandwich complexes of chalcogenated pyridine based bi-(N, S/Se) and terdentate (N, S/Se, N) ligands with (η^6-benzene)ruthenium(II) and the application of these complexes in the catalysis of transfer hydrogenation of ketones and oxidation of alcohols. The authors reported that the catalytic efficiency generally varies with chalcogen ligands in the order of Se > S, when other co-ligands and substituents on the donor atoms are the same. Another observation reported by the aforementioned authors is that the bidentate (Se, N) type ligand provides complexes with catalytic better efficiency. Prakash and co-workers[3c] also described efficient catalysis with the same kind of reaction using rhodium(III) and iridium(III) complexes of half-pincer chalcogenated pyridines as the catalytic system.

In light of these previous results and our interest in the unexplored coordination chemistry of the ligand 2-picolyl selenopyridine (**d**), we synthesized and characterized six new transition metal complexes (**1**, **2a–b**, **3–5**) and two complexes obtained as ligand decomposition products (**2c–d**) by IR, elemental analysis, electrospray ionization mass spectrometry and single-crystal X-ray crystallography.

The procedure used for the synthesis of ligand **L** is different from the one reported by Bhasin and co-workers[6] and afforded the product in good yield when compared with the literature.[6] For the synthesis of the ligand [$PySeCH_2Py$] **L**, the procedure described by Peglow and co-workers[1] was adapted using

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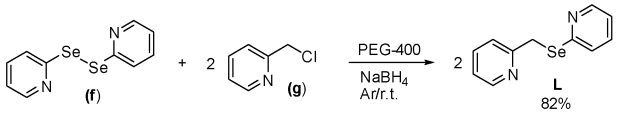
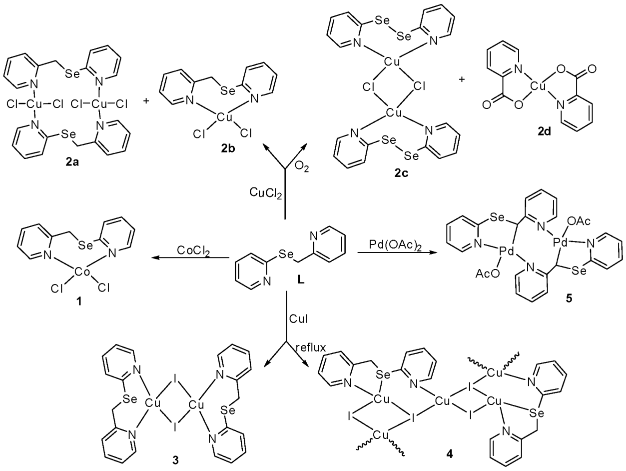


Scheme 1 Synthetic route for the synthesis of ligand **L**.

bis(2-pyridyl)diselenide (**f**), 2-(chloromethyl)pyridine (**g**), PEG-400 as the solvent and $NaBH_4$ as the reducing agent under an argon atmosphere for 3.5 h. The synthesis of **L** has been summarized in Scheme 1. The NMR spectra, elemental analysis and ESI^+MS data for ligand **L** are consistent with its structure which can also be seen and confirmed by the single-crystal X-ray diffraction studies of complexes **1–5**.

2-Picolyl selenopyridine **L** was used for complexation reactions with metal ions of different hardness (Co^{II}, Cu^{II}, Cu^I and Pd^{II}). Scheme 2 summarizes the reactions and their products. The complexes **1–5** obtained were characterized by single-crystal X-ray diffraction. Their molecular structures were designed with Diamond[8] and are shown in Fig. 2–9. The experimental part for the synthesis of the ligand (**L**) and complexes **1–5** and also crystallographic details are reported in the ESI.†

Complex [$CoCl_2$(**L**)] (**1**) was obtained when a solution of **L** (0.2 mmol) in 3 mL of dichloromethane was overlayered with a solution of $CoCl_2$ (0.2 mmol) in 3 mL of methanol. Slow diffusion of these solutions produced blue crystals of compound **1**. After three days, the crystals were collected and dried under a vacuum system. The ESI^+ mass spectra of the compound show intense peaks at m/z = 308.9329 for the molecular ion corresponding to $[C_{11}H_{10}CoN_2Se]^+$ (calc. 308.9341). In this complex, the 2-picolyl selenopyridine **L** acts as a bidentate ligand and is



Scheme 2 Synthetic routes used to obtain **1–5**.

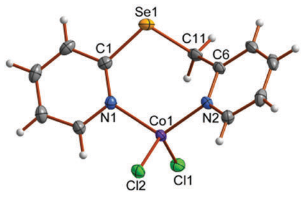


Fig. 2 Molecular structure of [$CoCl_2$(**L**)] (**1**). Thermal ellipsoids represent 30% probability.

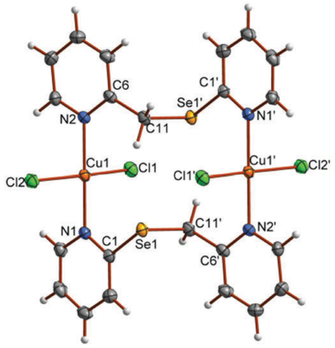


Fig. 3 Molecular structure of the binuclear copper(II) complex [Cu_2Cl_4(**L**)$_2$] (**2a**) with ellipsoids at the 30% probability level.

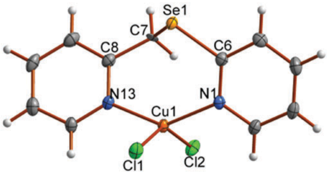


Fig. 4 Molecular structure of [$CuCl_2$(**L**)] (**2b**) with ellipsoids at the 50% probability level.

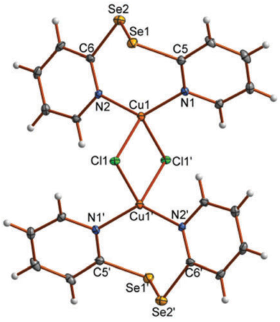


Fig. 5 Molecular structure of [$Cu_2Cl_2(PySe)_2$] (**2c**) with ellipsoids at the 50% probability level.

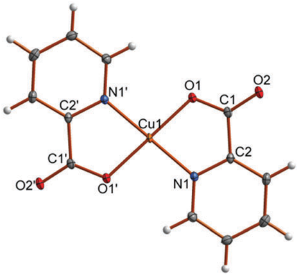


Fig. 6 Molecular structure of [Cu(2-PyCOO)$_2$] (**2d**) with ellipsoids at the 50% probability level.

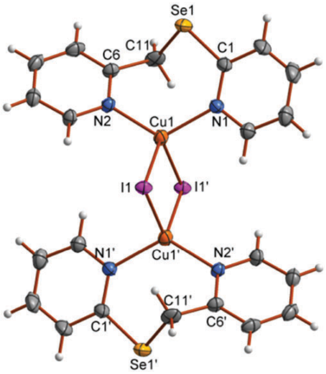


Fig. 7 Molecular structure of $[Cu_2I_2(\mathbf{L})_2]$ (**3**). Thermal ellipsoids represent 30% probability. Symmetry designator: (′) = 1 − x, 1 − y, −z.

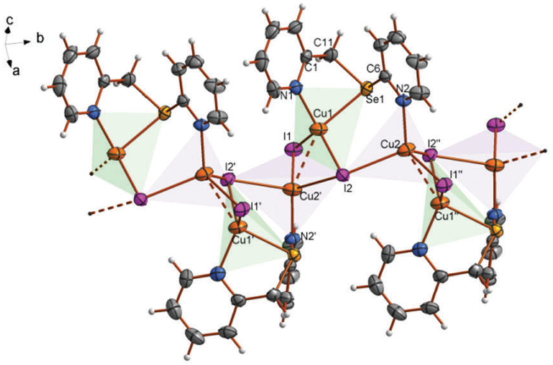


Fig. 8 Polymeric structure of $[Cu_2I_2(\mathbf{L})]_n$ (**4**). Thermal ellipsoids represent 30% probability. Symmetry designator: (′) = 1 − x, −0.5 + y, 1 − z; (″) = 1 − x, 0.5 + y, 1 − z.

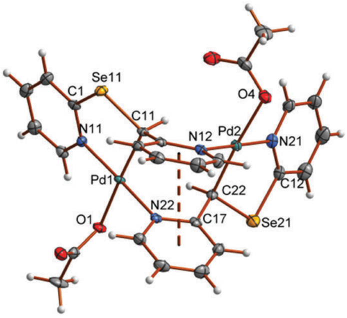


Fig. 9 Molecular structure of $[Pd_2(CH_3COO)_2(PySeCHPy)_2]\cdot 7H_2O$ (**5**). Thermal ellipsoids represent 50% probability. Water solvate molecules have been omitted for clarity.

coordinated with a cobalt metal atom through nitrogen atoms. In the crystal structure of $[CoCl_2(\mathbf{L})]$ (**1**), the Co^{II} adopts a typical tetrahedral geometry formed by two nitrogen atoms from the 2-picolyl selenopyridine ligand and two chlorine ligands, as shown in Fig. 2.

Compounds $[Cu_2Cl_4(\mathbf{L})_2]$ (**2a**) and $[CuCl_2(\mathbf{L})]$ (**2b**) were prepared in a way similar to that used for the synthesis of **1**, but using copper(II) chloride instead of cobalt(II) chloride. After some days, green (**2a**) and yellow (**2b**) crystals were observed in the mother liquor. An important difference was observed for the crystal yield of these compounds: **2a** 80.2% and **2b** 8.0%.

The molecular structure of **2a** (Fig. 3) shows a binuclear copper(II) complex, and the copper metal atom adopting a distorted square planar geometry. The ESI^+ mass spectrum of the compound shows an intense peak at m/z = 312.9319, which can be assigned to an ion of the composition $[C_{11}H_{10}CuN_2Se]^+$ (calc. 312.9305). Fig. 4 shows the molecular structure of complex **2b**. In this complex, the copper atom adopts a distorted tetrahedral geometry formed by two N atoms of the same ligand and two chloride ligands.

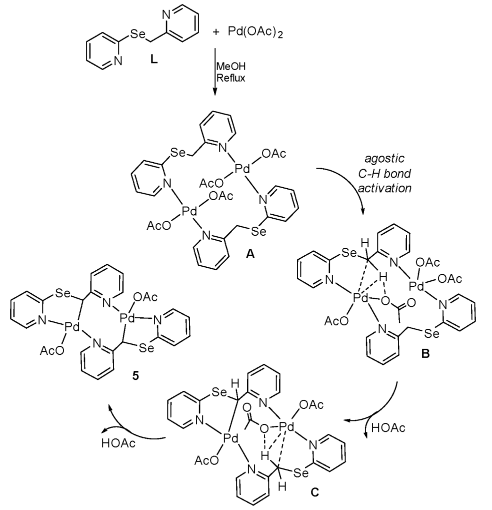
Trace amounts of the complexes $[Cu_2Cl_2(PySe)_2]$ (**2c**) and $[Cu(2\text{-}PyCOO)_2]$ (**2d**) were obtained as the by-products in the mother liquor of complexes **2a–b**. The orange (**2c**) and blue (**2d**) crystals were analyzed by single-crystal X-ray crystallography and the molecular structures are shown in Fig. 5 and 6, respectively.

Kienitz and collegues,[9] in 2000, described the synthesis of a [Cu(μ-Br)-(N,N′-PySeSePy)] complex that is structurally similar to complex **2c**. The molecular structure of **2c** shows a core with two copper(I) atoms being connected by two μ_2-chlorine atoms, in a tetrahedral geometry. This structure is different from the one obtained in the direct reaction between copper(II) chloride and bis(2-pyridil)diselenide (PySeSePy) described by our group[5a] in 2015. In the formation of these by-product complexes, the copper and selenium reduction (**2c**) and the oxidation of the alkyl carbon of the ligand **L** formed the carboxylate group (**2d**). The structure of the planar mononuclear copper(II) complex **2d** is well established in the literature.[10] In 2012, Wang and colleagues synthesized a picolinate copper(II) complex by promoting a reaction between $Cu(CH_3COO)_2\cdot H_2O$ and picolinic acid in a mixture of methanol and water as solvents. These authors also reported that this copper(II) complex shows typical intercalation with DNA, due to its nearly planar structure.

Complex $[Cu_2I_2(\mathbf{L})_2]$ (**3**) was obtained when a solution of **L** (0.2 mmol) in 3 mL of dichloromethane was overlayered with a solution of CuI (0.2 mmol) in 3 mL of methanol. Yellow crystals of **3** were obtained in the mother liquor reaction and a single-crystal was characterized by X-ray analysis. The structure of **3** (Fig. 7) shows a core with two copper atoms being connected by two μ_2-iodine atoms. Surrounding the core, four nitrogen atoms from two ligands **L** complete the tetrahedral coordination environment of the core. This coordination mode is similar to the one observed for compound **2c**.

The same starting material stoichiometry used to synthesize compound **3** was also used to obtain the polymer $[Cu_2I_2(\mathbf{L})]_n$ (**4**), but, in this reaction, the ligand **L** and copper(I) were solubilized in anhydrous methanol and stirred for 2 hours under reflux and an argon atmosphere. The ESI^+ mass spectrum of the compound shows an intense peak at m/z = 502.7662, which can be assigned to an ion of the composition $[C_{11}H_{10}Cu_2IN_2Se]^+$ (calc. 502.7646). The yellow crystals observed in the mother liquor were analyzed by X-ray crystallography and the structure obtained is represented in Fig. 8.

The one-dimensional polymeric chains grow along the crystallographic *b* axis. Each copper(I) atom adopted a distorted



Scheme 3 Mechanistic pathways proposed for the formation of $[Pd_2(CH_3COO)_2(PySeCHPy)_2]$ (**5**) through agostic C–H bond activation.

tetrahedral geometry, with the atoms of the ligands coordinating differently to the metal center. For example, the Cu2′ atom is coordinated by two μ_3-iodine, one μ_2-iodine and one N atom of the ligand **L** (Fig. 8 – light violet tetrahedron) and the Cu1 atom is coordinated by one μ_3-iodine, one μ_2-iodine, one N and one selenium atom of the same ligand **L** (Fig. 8 – light green tetrahedron). The observed copper-copper distances Cu1···Cu2′ and Cu2···Cu1″ of 2.6232 (7) Å can be interpreted as weak interactions and are shorter than the copper-copper distance reported for complex $[Cu_4I_4((2\text{-}PySe)_2CH_2)_2]$ 2.8481 (**3**).[3b] Among the complexes **1–5**, complex **4** was the only one in which the selenium soft atom coordinated with the copper(I) soft atom, and this complex was only formed when the reaction was performed under reflux conditions.

The cyclometallated palladium complex $[Pd_2(CH_3COO)_2(PySeCHPy)_2]\cdot 7H_2O$ (**5**) was obtained under reflux conditions by the reaction of $Pd(OAc)_2$ with the ligand **L** in methanol. The ESI$^+$ mass spectrum of the compound shows a peak at m/z = 769.8181, which can be assigned to an ion of the composition $[C_{24}H_{21}N_4O_2Pd_2Se_2 + H]^+$ (calc. 769.8137). Fig. 9 shows the molecular structure of **5** determined by single-crystal X-ray analysis. This complex is dimeric, with the palladium(II) atoms acquiring a distorted square planar geometry. The coordination around each palladium atom is defined by one O atom of the acetate ion, two N and one C atom of the metallated monoselenoethers. In this complex, one of the pyridyl rings on both the monoselenoether ligands are parallel to each other and are separated by 3.4690(2) Å, which may be attributed to π-stacking, according to the literature.[11a] Complex **5** has a palladium–carbon bond and the proposed mechanistic pathways for the formation of this compound, based on the literature,[11] is presented in Scheme 3. We believe that the first step involves the coordination of each palladium atom by two N atoms of the ligands (Scheme 3, structure A). In the remaining steps, considering the reported theoretical studies,[11] a five-membered intermediate (structures B and C) can be proposed. Both B and C structures are formed by agostic interactions between Pd and the benzilic C–H bond. The metallacycle formation (complex **5**) results from the C–H bond cleavage with the successive exclusion of HOAc and the formation of a C–Pd bond.

In summary, the syntheses of complexes **1–5** demonstrate the versatility of the ligand 2-picolyl selenopyridine (**L**) toward the formation of molecular, polymeric or cyclometallated complexes.

Compounds **1**, **2c**, **3**, **4** and **5** show that this class of ligand can stabilize metal centers at different oxidation levels, such as Co^{II}, Cu^{I} and Pd^{II}. It is well established that these transition metals in these oxidation states can be used in different organic reactions as a catalyst.[12] In metal catalysis systems it is important that the use of a ligand may increase the solubility of the metal salts in the solvents.[3a,b] Furthermore, it is reported[3e] that bidentate (Se, N) type ligands provide complexes with better catalytic efficiency.

Complexes **1**, **2c**, **3**, **4** and **5** allow us to predict its applications as a catalyst in coupling reactions. Some examples of reactions that use these transition metals as a catalyst are cross-dehydrogenative coupling[12d] (Co^{II}), cross-coupling reactions of arylboronic esters and aryl halides[12g] (Co^{II}), cross-coupling of iodobenzoates with bromozincdifluorophosphonate[12b] (Cu^{I}), Heck-type cross-coupling[12h] (Pd^{II}) and regioselective arylation of imidazoles[12i] (Pd^{II}).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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