



# Synthesis and characterization of new complexes derived from 4-thienyl substituted pyrimidines



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## ABSTRACT

The behavior of 4-thienyl substituted pyrimidine ligands ( $L^{1-3}$ ) has been studied for the series of their reactions with various salts of 3d metals (Co, Zn, Ni, Cu) and platinoids (Pt, Pd). In particular, mononuclear  $\text{Co}(\text{OTf})_2(L^{1-3})_2(\text{H}_2\text{O})_2(\text{MeCN})_2$  (**1**), binuclear  $\text{Co}_2(\text{Piv})_2(L^{1-3})_4$  (**2a,b**),  $\text{Cu}_2(\text{Piv})_2(L^{1-3})_2$  (**5a,b**), heterometallic polynuclear  $\text{Li}_2\text{Co}_2(\text{Piv})_6(L^{1-3})_2$  (**4**) and chelate  $[(L^1)\text{Pd}(\text{OAc})_2]$  (**6**) complexes have been obtained. The structures of all complexes have been established by X-ray diffraction. Also magnetic properties of coordination compounds **1**, **2**, **4** and **5** have been studied in details. In particular, mononuclear Co(II) complexes **1** and **4** proved to exhibit paramagnetism with large positive zero-field splitting parameters. Dinuclear Co(II) complexes **2a,b** show weak antiferromagnetic interactions. Dinuclear Cu(II) complexes **5a,b** demonstrate strong antiferromagnetic superexchange interactions via four carboxylate bridges. The systems **2a,b** and **5a,b** are isolated as exchange coupled dimers.

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## 1. Introduction

During the last decade the nitrogen-containing heterocycles have been used continuously as ligands in the coordinating chemistry [1]. This group of ligands includes the family of pyrimidines, which are known to have a great value in medicinal chemistry due to a variety of biological activity, ranging from antituberculosis [2], antiviral [3], antitumor [4], immunosuppressive [5], anticonvulsant to antioxidant [6] activities. Also, the excellent fluorescence properties of pyrimidines can be achieved by functionalization of the pyrimidine ring with phenylamine, carbazole, 2-phenylthiophene and 2,2'-bithiophene units [7,8]. The electron-withdrawing character of the pyrimidine ring, and the ability of nitrogen atoms for hydrogen bond formation allow pyrimidines to be attractive building blocks for the synthesis of conjugated polymers [9].

Pyrimidine, as monodentate ligand, has been used for the synthesis of a variety of transition metal complexes of different nuclearities [10]. Due to the presence of two nitrogen lone pairs the

pyrimidine unit can form a bridge between two metal atoms, thus making possible the formation of not only coordination polymers [11], but also pyrimidine-bridged binuclear species [12]. A variety of the coordination modes in these chelate complexes can be achieved by using pyrimidines, bearing the imine (Schiff base) [13], sulfanyl [14] and azomethine [15] functional groups, pyrazolyl- [16], pyridinyl- [17] and triazolylpyrimidine [18] ligands, as well as pyrimidine functionalized N-heterocyclic carbenes [19] or annulated pyrimidines [20]. However, examples of cyclometalated complexes on the basis of (het)arylsubstituted pyrimidines are rather limited [21]. Meanwhile, the synthesis of transition metal complexes, exhibiting magnetic, photochemical properties and biological activity, is a great value for both material science and pharmacology. Indeed, a number of pyrimidine complexes are characterized by antiferromagnetic [11d,22,23] and ferromagnetic [23] behavior, while others have been investigated as antiparasitic [24], anti-inflammatory [25], antitumor [26], antibacterial [27] agents.

In this paper we wish to report the data concerning complexation behavior of the earlier described fluorescent 4-(thienyl)pyrimidines [8] toward several metal ions. 4-(Thienyl)- and 4,5-di(thienyl) substituted pyrimidines ( $L^{1-3}$ )

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proved to act as monodentate ligands in the reactions with  $[\text{Cu}_2(\text{Piv})_4]_n$  (Piv is the pivalate anion),  $[\text{Co}(\text{Piv})_2]_n$  and  $\text{Co}(\text{OTf})_2 \cdot 6\text{H}_2\text{O}$  (Otf is the triflate anion). One mononuclear complex,  $[\text{Co}(\text{L}^1)_2(\text{H}_2\text{O})_2(\text{MeCN})_2] \cdot 2\text{OTf}$  (**1**), two binuclear complexes having similar structures,  $[\text{Co}_2(\text{Piv})_2(\text{L}^{1,2})_2]$  (**2a,b**) and  $[\text{Cu}_2(\text{Piv})_2(\text{L}^{2,3})_2]$  (**5a,b**), and one lithium-containing bimetallic complex with cobalt  $[\text{Li}_2\text{Co}_2(\text{Piv})_6(\text{L}^2)_2]$  (**4**) have been synthesized and their magnetic properties have been elucidated.

There is a great interest in the synthesis of cyclometalated platinum(II) and iridium(III) complexes with (oligo)thienylpyrimidines due to their luminescent properties [28]. Based on the known examples of cyclometalated complexes with naphthalenylpyrimidine [21], and taking into account some similarity between pyrimidine and pyridine coordinative properties, we have assumed the ability of 4-(thienyl)pyrimidines to form cyclometalated Pd(II) and Pt(II) complexes. However, the only C,N-coordinated palladacyclic dimer, deriving from 4-(2-thienyl)pyrimidine ( $\text{L}^1$ ) and palladium acetate, has been synthesized and characterized by the data of IR,  $^1\text{H}$  NMR spectroscopy and single crystal X-ray diffraction.

## 2. Materials and methods

### 2.1. Methods and synthesis

The starting materials  $[\text{Co}(\text{OTf})_2] \cdot 6\text{H}_2\text{O}$  [29],  $[\text{Co}(\text{Piv})_2]_n$  [30],  $[\text{Cu}_2(\text{Piv})_4]_n$  [31], LiPiv [32], 4-(2-thienyl)pyrimidine ( $\text{L}^1$ ), 4-[2,2']-(bithiophen-5-yl)-pyrimidine ( $\text{L}^2$ ), and 4-[2,2']-(bithiophen-5-yl)-5-(thien-2-yl)pyrimidine ( $\text{L}^3$ ) [8] have been prepared according to the previously reported procedures. The following solvents, MeCN, THF,  $\text{CH}_2\text{Cl}_2$  and 1,4-dioxane, as well as  $\text{Pd}(\text{OAc})_2$  (>99%, Sigma–Aldrich) were used without additional purification.

Melting points were determined on Boetius combined heating stages and were not corrected. Elemental analysis was carried on a Eurovector EA 3000 automated analyzer. The  $^1\text{H}$  NMR spectra were recorded on an AVANCE-500 instruments using  $\text{Me}_4\text{Si}$  as an internal standard. IR spectra of the complexes were recorded on a Spectrum One Fourier transform IR spectrometer (Perkin Elmer) equipped with a diffuse reflectance attachment (DRA) in the frequency range  $450\text{--}3700\text{ cm}^{-1}$ . Spectrum processing and band intensity determination were carried out using the special software supplied with the spectrometer.

#### 2.1.1. $[\text{Co}(\text{L}^1)_2(\text{H}_2\text{O})_2(\text{MeCN})_2] \cdot 2\text{OTf}$ (**1**)

4-[2,2']-Bithiophen-5-yl-pyrimidine ( $\text{L}^2$ ) (0.1 g, 0.409 mmol) was dissolved in tetrahydrofuran (5 mL) and added to a solution of  $[\text{Co}(\text{OTf})_2] \cdot 6\text{H}_2\text{O}$  (0.095 g, 0.409 mmol) in MeCN (15 mL). The brown reaction mixture was then stirred at 50–60 °C for 2 h. Slow evaporation of the solvent gave brown prismatic crystals suitable for X-ray diffraction, which were separated from the solution by decantation and washed with a cold MeCN. Yield: 0.2 g, 95%. Found: C, 41.75; H, 3.74; N, 8.16. Calc. for  $\text{C}_{36}\text{H}_{32}\text{CoF}_6\text{N}_6\text{O}_8\text{S}_6$ : C, 41.50; H, 3.96; N, 8.06%. FT-IR (DRA,  $\text{cm}^{-1}$ ): 3510, 3400, 3240, 3135, 3089, 2924, 2829, 1633, 1599, 1533, 1514, 1464, 1448, 1423, 1397, 1319, 1302, 1220, 1192, 1089, 1070, 1036, 1017, 843, 800, 737, 690, 665, 641, 577, 516, 454.

#### 2.1.2. $[\text{Co}_2(\text{Piv})_2(\text{L}^1)_4]$ (**2a**)

Tetrahydrofuran (20 mL) was added to a mixture of  $[\text{Co}(\text{Piv})_2]_n$  (0.1 g, 0.406 mmol) and 4-(2-thienyl)-pyrimidine ( $\text{L}^1$ ) (0.077 g, 0.406 mmol). The brown reaction mixture was heated at 60 °C for 2 h, followed by solution was concentrated to 10 mL and cooled to room temperature. Brown crystals precipitated after 2 days were separated from the solution by decantation, washed with cold THF, and dried. Yield: 0.275 g, 90%. Found: C, 53.21; H, 5.19;

N, 9.46. Calc. for  $\text{C}_{52}\text{H}_{60}\text{Co}_2\text{N}_8\text{O}_8\text{S}_4$ : C, 53.33; H, 5.16; N, 9.57%. FT-IR (DRA,  $\text{cm}^{-1}$ ): 3073, 2962, 1587, 1536, 1482, 1463, 1422, 1392, 1363, 1311, 1277, 1247, 1227, 1188, 1165, 1082, 1012, 986, 897, 856, 828, 808, 795, 786, 773, 732, 716, 666, 631, 623, 603, 456.

#### 2.1.3. $[\text{Co}_2(\text{Piv})_2(\text{L}^2)_4]$ (**2b**)

*Method A:* Tetrahydrofuran (20 mL) was added to a mixture of  $[\text{Co}(\text{Piv})_2]_n$  (0.1 g, 0.406 mmol) and 4-[2,2']-bithiophen-5-yl-pyrimidine ( $\text{L}^2$ ) (0.54 g, 0.203 mmol). The brown reaction mixture was heated at 60 °C for 2 h, followed by solution was concentrated to 10 mL and cooled to room temperature. A mixture of brown and dark purple crystals were grown after 1 day from the reaction solution. According to the X-ray analysis the brown crystals proved to correspond to **2b**, while the dark purple crystals were identified as  $[\text{Co}(\text{Piv})(\text{L}^2)]_4$  (**3**).

*Method B:* The solvent (MeCN) was dried and purified according to the procedure described earlier [33]. A solution of 4-[2,2']-bithiophen-5-yl-pyrimidine ( $\text{L}^2$ ) (0.54 g, 0.203 mmol) in a freshly distilled MeCN (10 mL) was degassed with argon for 30 min.  $[\text{Co}(\text{Piv})_2]_n$  (0.1 g, 0.406 mmol) was added to the solution. The brown reaction mixture was heated at reflux under argon for 1 h and cooled down to a room temperature. The brown crystals formed in 1 day were separated from the solution by decantation, washed with MeCN, and dried. Yield: 0.243 g, 80%. Found: C, 54.26; H, 4.56; N, 7.35. Calc. for  $\text{C}_{68}\text{H}_{68}\text{Co}_2\text{N}_8\text{O}_8\text{S}_8$ : C, 54.46; H, 4.57; N, 7.47%. FT-IR (DRA,  $\text{cm}^{-1}$ ): 3103, 3073, 3055, 1969, 1774, 1641, 1615, 1582, 1536, 1516, 1469, 1448, 1425, 1394, 1364, 1305, 1277, 1240, 1229, 1205, 1172, 1084, 1048, 994, 981, 886, 839, 792, 769, 744, 726, 711, 697, 672, 660, 615, 596, 505, 458.

#### 2.1.4. $[\text{Li}_2\text{Co}_2(\text{Piv})_6(\text{L}^2)_2]$ (**4**)

A mixture of  $[\text{Co}(\text{Piv})_2]_n$  (0.107 g, 0.409 mmol), 4-[2,2']-bithiophen-5-yl-pyrimidine ( $\text{L}^2$ ) (0.1 g, 0.409 mmol), and LiPiv (0.044 g, 0.409 mmol) was heated in THF (30 mL) at 60 °C for 30 min. THF was evaporated and precipitate obtained was dissolved in 1,4-dioxane (15 mL). The violet crystals suitable for X-ray diffraction were grown by evaporation of solvent at 60 °C up to 1 mL and further holding at room temperature. Yield: 0.176 g, 70%. Found: C, 53.60; H, 8.81; N, 2.85. Calc. for  $\text{C}_{54}\text{H}_{70}\text{Co}_2\text{Li}_2\text{N}_4\text{O}_{12}\text{S}_4$ : C, 52.86; H, 5.75; N, 4.57%. FT-IR (DRA,  $\text{cm}^{-1}$ ): 3106, 3072, 2962, 2869, 1584, 1549, 1512, 1482, 1460, 1409, 1363, 1309, 1260, 1225, 1191, 1094, 1012, 865, 842, 791, 735, 702, 662, 616, 571, 456.

#### 2.1.5. $[\text{Cu}_2(\text{Piv})_2(\text{L}^{2,3})_2]$ (**5a, 5b**)

4-[2,2']-Bithiophen-5-yl substituted pyrimidine ( $\text{L}^2$  or  $\text{L}^3$ ) (0.409 mmol) was dissolved in THF (5 mL) and added to a solution of  $[\text{Co}(\text{OTf})_2] \cdot 6\text{H}_2\text{O}$  (0.095 g, 0.409 mmol) in MeCN (15 mL). The reaction mixture was stirred at 50–60 °C for 2 h. Slow evaporation of the solvent gave green prismatic crystals of **5a** (Fig. 6) and **5b** (Fig. 7), respectively.

**5a:** Yield: 0.193 g, 93%. Found: C, 51.95; H, 5.22; N, 5.63. Calc. for  $\text{C}_{44}\text{H}_{52}\text{Cu}_2\text{N}_4\text{O}_8\text{S}_4$ : C, 51.80; H, 5.14; N, 5.49%. FT-IR (DRA,  $\text{cm}^{-1}$ ): 3109, 2957, 2925, 1614, 1587, 1538, 1516, 1481, 1464, 1417, 1397, 1374, 1360, 1307, 1279, 1225, 1186, 1083, 1068, 1045, 1013, 895, 840, 798, 789, 766, 732, 709, 662, 618, 440.

**5b:** Yield: 0.214 g, 89%. Found: C, 54.46; H, 4.57; N, 7.47. Calc. for  $\text{C}_{52}\text{H}_{56}\text{Cu}_2\text{N}_4\text{O}_8\text{S}_6$ : C 54.26; H, 4.56; N, 7.35%. FT-IR (DRA,  $\text{cm}^{-1}$ ): 3105, 3090, 3071, 3013, 1565, 1540, 1509, 1454, 1430, 1390, 1347, 1325, 1279, 1228, 1204, 1186, 1168, 1120, 1078, 1071, 1052, 1038, 984, 951, 932, 886, 838, 808, 783, 755, 740, 419, 699, 663, 605, 588, 559, 536, 516, 484.

#### 2.1.6. $[(\text{L}^1)\text{Pd}(\text{OAc})_2]$ (**6**)

A mixture of 4-(2-thienyl)pyrimidine ( $\text{L}^1$ ) (0.162 g, 1 mmol) and  $\text{Pd}(\text{OAc})_2$  (0.225 g, 1 mmol) in AcOH (5 mL) was stirred for 3 h at on

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