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# Unprecedented Layered Coordination Polymers of Dithiolene Group 10 Metals. Magnetic and Electrical Properties

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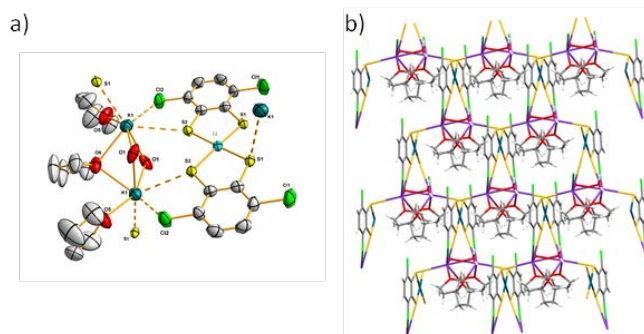
One-pot reactions between Ni(II), Pd(II) or Pt(II) salts and 3,6-dichloro-1,2-benzenedithiol (HSC<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>SH) in KOH medium under argon, lead to a series of bis-dithiolene coordination polymers. X-ray analysis shows the presence of a common square planar complex [M(SC<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>S)<sub>2</sub>]<sup>2-</sup> linked to potassium cations forming either a two-dimensional coordination polymer network for {[K<sub>2</sub>(μ-H<sub>2</sub>O)<sub>2</sub>(μ-thf)(thf)<sub>2</sub>][M(SC<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>S)<sub>2</sub>]}<sub>n</sub> [M = Ni (**1**) and Pd (**2**)] or a one-dimensional coordination polymer for {[K<sub>2</sub>(μ-H<sub>2</sub>O)<sub>2</sub>(thf)<sub>6</sub>][Pt(SC<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>S)<sub>2</sub>]}<sub>n</sub> (**3**). In **3** the coordination environment of the potassium ions may slightly change leading to the two-dimensional coordination polymer {[K<sub>2</sub>(μ-H<sub>2</sub>O)(μ-thf)<sub>2</sub>][Pt(SC<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>S)<sub>2</sub>]}<sub>n</sub> (**4**) that crystallizes together with **3**. The physical characterization of compounds **1-3** show similar trends, they are diamagnetic and behave as semiconductors.

## Introduction

The interesting electronic and structural properties, as well as the biological role shown by transition metal dithiolene complexes, has motivated a great deal of research in this field.<sup>1-15</sup> Dithiolenes are classified as “non-innocent” ligands since they can form complexes in different oxidation states and as a consequence they can have different magnetic moments and electronic configurations. In fact, formation of neutral, monoanionic and dianionic dithiolene complexes is well-reported.<sup>16-18</sup> In this type of derivatives the M-C, C-C and S-C bond lengths are strongly dependent on the redox state. Additionally, it is well-known that the presence of coordinating substituents in the aromatic rings of the dithiolene ligands may favour the formation of in the transition metal coordination polymers (CPs). Although many dithiolene derivatives of group 10 metals forming discrete molecules such as [Na(N15C5)<sub>2</sub>][Pd(mnt)<sub>2</sub>] (mnt = 1,2-dicyanoethylene-1,2-dithiolate),<sup>19</sup> (MePh<sub>3</sub>P)[Ni(bdt)<sub>2</sub>] (bdt = 1,2-benzenedithiolate),<sup>20</sup> (MePh<sub>3</sub>P)[Ni(bdtCl<sub>2</sub>)<sub>2</sub>] (bdtCl<sub>2</sub> = 3,6-dichloro-1,2-benzenedithiolate),<sup>20</sup> or supramolecular networks as [K(N18C6)]<sub>2</sub>[M(i-mnt)<sub>2</sub>] (M= Ni, Pd, Pt; i-mnt = 1,1-dicyanoethylene-2,2-dithiolate),<sup>19</sup> {[K(N18-C6)]<sub>2</sub>(CH<sub>3</sub>CN)}[Ni(mnt)<sub>2</sub>],<sup>21</sup> [K(18-crown-6)][Ni(α-tpdt)<sub>2</sub>] (α-tpdt

= 2,3-thiophene dithiolate),<sup>22</sup> [K(DC18C6-B)]<sub>4</sub>[Pt(mnt)<sub>2</sub>]<sub>2</sub><sup>23</sup> have been described, little is still known on dithiolene-based CPs where the network organization is based on the use of coordination bonds. Indeed, this is still limited to one-dimensional CPs such as: [Na(N15C5)]<sub>2</sub>[Pt(i-mnt)<sub>2</sub>],<sup>24</sup> [Na(N15C5)]<sub>2</sub>[Pd(i-mnt)<sub>2</sub>],<sup>19</sup> [K(DC18C6-A)]<sub>2</sub>[M(mnt)<sub>2</sub>] (M = Ni, Pd and Pt),<sup>25</sup> [K(DC18C6-A)]<sub>2</sub>[Pt(i-mnt)<sub>2</sub>],<sup>26</sup> {[Na(benzo-15-crown-5)]<sub>2</sub>Ni(i-mnt)<sub>2</sub>}]<sub>n</sub>·nCH<sub>2</sub>Cl<sub>2</sub>, {[Na(benzo-15-crown-5)]<sub>2</sub>Ni(mnt)<sub>2</sub>}]<sub>n</sub>,<sup>27</sup> {[CuL<sup>1</sup>]<sub>2</sub>Gd(O<sub>2</sub>NO)Ni(mnt)<sub>2</sub>·CH<sub>3</sub>OH·CH<sub>3</sub>CN}, {[CuL<sup>1</sup>]<sub>2</sub>Sm(O<sub>2</sub>NO)Ni(mnt)<sub>2</sub>·2CH<sub>3</sub>CN} (L<sup>1</sup> = N, N'-propylene-di(3-methoxysalicylideneiminato)).<sup>28</sup> However, to our knowledge no examples of 2D coordination polymer containing group 10 metal dithiolene entities have been yet described.

In this context, we have recently reported a series of 1D CPs consisting on the dianionic moieties [Fe<sub>2</sub>(SC<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>S)<sub>4</sub>]<sup>2-</sup> bridged by alkaline-metal complexes.<sup>29</sup> These CPs have shown interesting electrical properties together with a rich structural variety.



**Figure 1.** (a) ORTEP of {[K<sub>2</sub>(μ-H<sub>2</sub>O)<sub>2</sub>(μ-thf)(thf)<sub>2</sub>][Ni(SC<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>S)<sub>2</sub>]}<sub>n</sub> (**1**). (b) Representation of the bidimensional network of {[K<sub>2</sub>(μ-H<sub>2</sub>O)<sub>2</sub>(μ-thf)(thf)<sub>2</sub>][Ni(SC<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>S)<sub>2</sub>]}<sub>n</sub> (**1**).

Herein we describe the synthesis, structural characterization and the magnetic and electronic conductivity studies of a series

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† Additional experimental data and X-ray crystallographic files in CIF format for compounds **1-4** are provided (CCDC refs.: 1450245-1450248). Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

of 1D and 2D coordination polymers of Ni(II), Pd(II) and Pt(II) prepared with the dithiolate ligand  $(SC_6H_2Cl_2S)_2^{2-}$ .

## Results and discussion

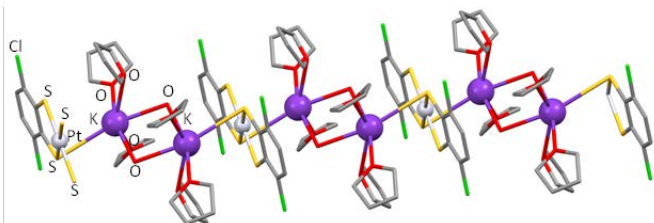
### Synthesis and Structural Characterization

The direct reaction between  $NiCl_2 \cdot 6H_2O$ ,  $Pd(OAc)_2$  or  $K_2PtCl_4$  and  $1,2-HSC_6H_2Cl_2SH$  in presence of KOH leads to the isolation of compounds  $\{[K_2(\mu-H_2O)_2(\mu-thf)(thf)_2][M(SC_6H_2Cl_2S)_2]\}_n$  [ $M = Ni$  (**1**) and  $Pd$ (**2**)] or  $\{[K_2(\mu-H_2O)_2(thf)_6][Pt(SC_6H_2Cl_2S)_2]\}_n$  (**3**), respectively.

**Table 1.** Selected average bond distances (Å) for compounds 1-4.

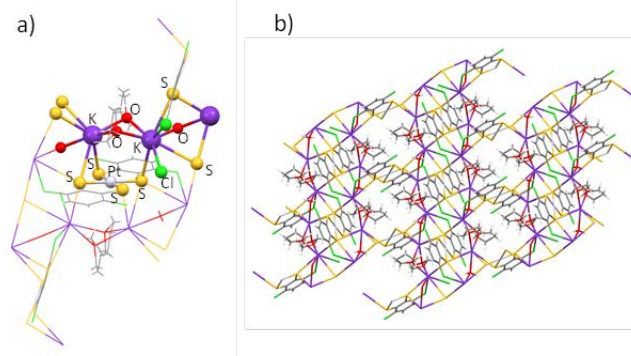
Compound	1	2	3	4
C=C	1.39(1)	1.42 (2)	1.415(6)	1.39(1)
C-S	1.757(1)	1.712(11)- 1.757(10)	1.766(4)	1.760(5)
M-S	2.175(1)	2.283(4)	2.305(4)	2.273(3)- 2.300(3)
K-O <sub>thf</sub>	2.684(6)- 2.805(6)	2.679(9)- 2.828(9)	2.702(4)- 2.858(4)	2.834(9)
K-O <sub>wat</sub>	2.778(2)	2.763(4)	2.808(4)- 2.841(3)	2.717(9)
K-Cl	3.388(3)	3.457(4)	-	3.317(4)- 3.543(4)
K-S	3.414(3)- 3.482(3)	3.390(4)- 3.497(4)	3.407(2)	3.169(4)- 3.694(4)

The crystal structures of **1** and **2** are shown in Figure 1 and S1, and a selection of bond distances are collected in Table 1. Both compounds are almost isostructural and consist of monomeric metal complexes  $[M(SC_6H_2Cl_2S)_2]^{2-}$  [ $M = Ni$  (**1**) and  $Pd$ (**2**)] bridged by dimetallic  $[K_2(\mu-H_2O)_2(\mu-thf)(thf)_2]^{2+}$  units *via* K-S and K-Cl bonds, leading to a two-dimensional coordination polymer network formulated as  $\{[K_2(\mu-H_2O)_2(\mu-thf)(thf)_2][M(SC_6H_2Cl_2S)_2]\}_n$  [ $M = Ni$  (**1**),  $Pd$  (**2**)] (Figures 1b and S1). The metal centres are coordinated by two dithiolato ligands in an almost square-planar geometry. The M-S, C-S, C=C and C-C bond lengths (Table 1) are in the range found in other bis-dithiolene nickel(II) and palladium(II) derivatives.<sup>19, 27, 30-32</sup> The dimetallic units are formed by two potassium atoms bridged by two  $H_2O$  molecules and a thf ligand. Each potassium is also linked to two sulphur atoms of dithiolene ligands, as well as to a terminal thf and a chloride atom of a dithiolene. The coordination environment of each potassium centre can be considered as a highly distorted monocapped octahedron.



**Figure 2.** View of a chain of compound  $[K_2(\mu-H_2O)_2(thf)_6][Pt(SC_6H_2Cl_2S)_2]_n$  **3**.

Figure 2 displays a view of compound **3** which consists of monomeric platinum(II) bis-dithiolato moieties bridged by dipotassium complexes leading to a 1D-CP chain. The dipotassium entity is based on two  $H_2O$  bridging ligands, six terminal thf and two sulphur atom of different dithiolene ligands. The platinum atoms exhibit the expected square planar geometry (S-Pt-S 180 ° and Pt-S 2.310 and 2.301 Å, Table 1).



**Figure 3.** (a) View of the basic building blocks of compound  $\{[K_2(\mu-H_2O)_2(\mu-thf)(thf)_2][Pt(SC_6H_2Cl_2S)_2]\}_n$  **4**. (b) Representation of a layer showing the connections between the Pt(II) bis-dithiolene complexes and the potassium chains.

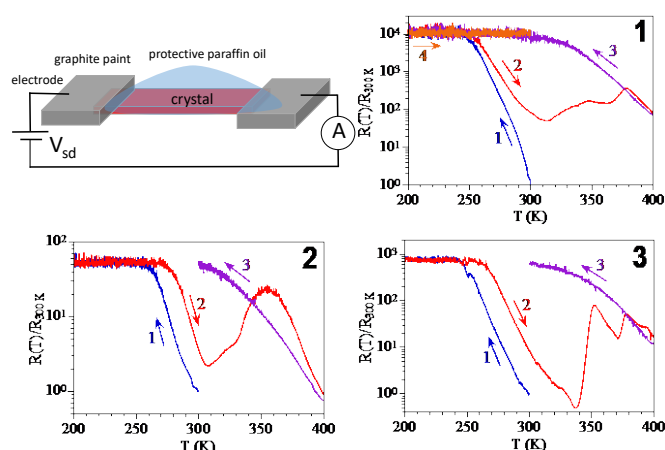
Compound **3** crystallizes together with traces amount of crystals corresponding to compound  $\{[K_2(\mu-H_2O)_2(\mu-thf)(thf)_2][Pt(SC_6H_2Cl_2S)_2]\}_n$  **4**. The structure of **4** is displayed in Figure 3. Compound **4** consists of layers formed by potassium *zig-zag* chains connected by monomeric  $[Pt(SC_6H_2Cl_2S)_2]^{2-}$  entities (Figure 3b). The potassium chains are formed by two different potassium entities. One potassium centre connects with four sulphur atoms of two neighbouring bis-dithiolene Pt(II) entities. The coordination sphere is completed by two thf and a water molecule bridging K atoms. The other potassium centre is linked to three sulphur and two chlorine atoms of different dithiolene ligands, finally a water molecule and two thf bridging ligands complete the coordination sphere. A distorted pentagonal bipyramid and a highly distorted bicapped octahedron geometries is found around the two different potassium centres (Figure 3a).

As far as we know, layers of dithiolene-containing coordination polymers with group 10 metals and alkaline metals have not been described to date. In fact, the only reported dithiolene derivatives of group 10 metals are  $\{[Na(\text{benzo-15-crown-5})]_2[Ni(i\text{-mnt})_2]_n \cdot nCH_2Cl_2\}$ ,<sup>27</sup>  $\{[Na(\text{benzo-15-crown-5})]_2[Ni(\text{mnt})_2]_n\}$ ,<sup>27</sup>  $[Na(N15C5)]_2[Pd(i\text{-mnt})_2]$ ,<sup>19</sup>  $[K(\text{DC18C6-A})]_2[Pt(i\text{-mnt})_2]$ ,<sup>26</sup> and  $[K(\text{DC18C6-A})]_2[M(\text{mnt})_2]$  ( $M = Ni, Pd, Pt$ ).<sup>25</sup> All of them form monodimensional structures through Na-N and K-N bonds between anionic and cationic entities.

### Physical Properties

The physical characterization of compounds **1-3** shows that these compounds present similar trends. The electrical conductivity measurements of compounds **1-3** show that these compounds are initially semiconductors with room temperature conductivity values of  $10^{-6}$  to  $10^{-7} \text{ Scm}^{-1}$  (Table 2). When the samples are cooled, the resistivity sharply increases

and below *ca.* 250 K it reaches the measuring limit of our equipment ( $5 \times 10^{11} \Omega$ ) (Figure 4).



**Figure 4.** The scheme used for the conductivity measurements (upper left), and thermal variation of the normalized resistance of compounds **1-3** during different thermal scans.

This sharp increase in the case of sample **1** leads to an unusually high activation energy of *ca.* 2200 meV, much higher than the values found in **2** and **3** (*ca.* 900 meV, Figure S2). Additionally, in the first heating scan, sample **1** does not recover the original room temperature value but a value two orders of magnitude higher. All these data suggest that the sharp increase must be due to a continuous solvent lost taking place at room temperature in sample **1** (probably due to an incomplete protection of the paraffin oil since other single crystals of this compound do not show such abrupt increase in the first cooling scan). When the samples are heated from 200 K they show the expected decrease of the resistivity with increasing temperature although with a hysteresis of *ca.* 10-20 K that cannot be attributed to the thermal equilibrium of the sample (less than 2 K at the used scan rate of 1 K min<sup>-1</sup>). This thermal hysteresis is observed in all the crystals of the three samples and might be attributed to the thermal insulating effect of the paraffin oil used to protect the crystals. On further heating, all the samples show minima in the resistivity at 313, 308 and 338 K in **1-3**, respectively (Figure 4). Above these temperatures the resistivity increases and reaches maxima at *ca.* 378, 355 and 353 K for **1-3**, respectively (Figure 4). Rather than to a metallic behaviour of the samples at high temperatures, the increase observed when heating the crystals at high temperatures has to be attributed to a degradation of the sample as confirmed by the irreversibility of the first heating scan. Thus, after heating the sample at 400 K the cooling scan shows a much higher resistivity (the resistance reaches the limit of our equipment at *ca.* 300 K) and a classical semiconducting behaviour with activation energies of *ca.* 880, 720 and 920 meV in **1-3**, respectively (Table 2, Figure S2). In sample **1** we performed an additional cooling scan down to 200 K followed by a heating scan to 300 K that confirms this irreversible effect. As expected from their similar structures, the three compounds show similar average room temperature conductivities, all in the  $10^{-6}$  to  $10^{-7}$  Scm<sup>-1</sup> range (Table 2).

As already mentioned, compounds **1-3** are very sensitive to the temperature and easily undergo degradation due to partial loss of some coordinated thf molecules, as confirmed by elemental microanalysis (see Experimental Section). This solvent loss is also clearly observed by changes in the crystal colour and by the appearance of micro-fractures in the crystals.

**Table 2.** Electrical conductivity values and activation energies of compounds **1-3**.

Compound	$\sigma_{300}$ (S/cm)	Ea (meV)
<b>1</b>	$1 \times 10^{-6}$	880
<b>2</b>	$3 \times 10^{-6}$	720
<b>3</b>	$2 \times 10^{-7}$	920

The magnetic susceptibility measurements of all the compounds confirm that they are diamagnetic (Figure S3), as expected since square planar d<sup>8</sup> ions present a S = 0 spin ground state.

## Experimental

All reactions were carried out under argon atmosphere. All reagents and solvents are commercial and were used as received without further purification. Elemental analyses were performed on an LECO CHNS-932 Elemental Analyser.

**X-ray structure analysis of 1-4.** Single crystals of compounds **1-4** were covered with a layer of a viscous perfluoropolyether (Fomblin®Y), mounted on a cryoloop™ with the aid of a microscope and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit and with a graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved using the WINGX<sup>33</sup> package by direct methods (SHELXS-97 for **1** and **4**, SHELXS-2013 for **2** and SHELXT-2014 for **3**<sup>34, 35</sup> and refined by least-squares against F<sup>2</sup> (SHELXL-2014 for **1**, **2** and **3**, and SHELXL-2013 for **4**). Compounds **1** and **2** were both studied with the C2/c space group. After the solution and refinement, and using the TwinRotMat procedure of the PLATON package,<sup>36</sup> we found a situation of merohedral twinning for them. The optimization of the BASF parameter in the refinement let us to obtain a 12 % contribution for the second component in **1** and 18 % in compound **2**. Furthermore, the poor quality of crystals in the case of **1** forced us to use a constrained refinement for the carbon atoms of the C51-C54 thf molecule.

All non-hydrogen atoms were anisotropically refined except C61 in compound **2** that could only be isotropically refined. The hydrogen atoms were positioned geometrically and refined using a riding model. The crystal data is shown in Table S1.

The thermal dependence of the DC electrical conductivity was measured with the two contacts method on different single crystals of compounds **1-3**. Crystals of compounds **1-3** were measured in three or four consecutive scans: they were initially cooled from 300 to 200 K (since below this temperature the resistance was above the limit of our equipment,  $5 \times 10^{11} \Omega$ ), then heated from 200 to 400 K and then cooled again from 400 to 200 or 300 K. The contacts were made with Pt wires (25  $\mu\text{m}$  diameter) using graphite paste. The samples were measured in

a Quantum Design PPMS-9 equipment connected to an external voltage source (Keithley model 2450 source-meter) and amperometer (Keithley model 6514 electrometer). Since all the crystals loose crystallinity very fast, the crystals were covered with paraffin oil immediately after the contacts were done. All the conductivity quoted values have been measured in the voltage range where the crystals are Ohmic conductors. The cooling and warming rates were 1 and 2 K min<sup>-1</sup>.

Magnetic measurements were performed with a Quantum Design MPMS-XL-5 SQUID magnetometer in the temperature range 2-300 K with a magnetic field of 0.5 on polycrystalline samples of compounds **1-3**, all kept with their mother liquor (with dry masses of 16.71, 13.65 and 10.30 mg, respectively). Susceptibility data were corrected for the sample holder and for the diamagnetic contribution of the salts using Pascal's constants.<sup>37</sup>

**Synthesis of compounds  $\{[K_2(\mu-H_2O)_2(\mu-thf)(thf)_2][M(SC_6H_2Cl_2S)_2]\}_n$  [M = Ni (**1**) and Pd (**2**)].** A mixture of 1,2-HSC<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>SH (266 mg, 1.27 mmol) and 10 mL of a 5 % aqueous solution of KOH was stirred for 5 min. Then, a solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (150 mg, 0.63 mmol) in 10 mL of EtOH/H<sub>2</sub>O (1:1) was slowly added. After 30 min. stirring at room temperature, the solvent was removed in vacuum, yielding a solid residue which was washed with *n*-hexane. Recrystallization of the solid in wet thf/*n*-heptane at room temperature yielded crystals suitable for X-ray analysis of compound  $\{[K_2(\mu-H_2O)_2(\mu-thf)(thf)_2][Ni(SC_6H_2Cl_2S)_2]\}_n$  **1** (328 mg, 64.5 % yield). All the solvents used in the synthetic and crystallization processes were previously deoxygenated. Anal. Calcd. (Found) for C<sub>16</sub>H<sub>16</sub>Cl<sub>4</sub>K<sub>2</sub>NiO<sub>3</sub>S<sub>4</sub>: C, 28.97 (27.53); H, 2.43 (2.15); S, 19.34 (19.19) %.

Following the same procedure but using Pd(OAc)<sub>2</sub> as starting material, suitable crystals for X-ray diffraction analysis of compound  $\{[K_2(\mu-H_2O)_2(\mu-thf)(thf)_2][Pd(SC_6H_2Cl_2S)_2]\}_n$  **2** (229 mg, 39.9%) were obtained from a solution of wet thf/*n*-heptane at room temperature. Anal. Calcd. (Found) C<sub>16</sub>H<sub>16</sub>Cl<sub>4</sub>K<sub>2</sub>O<sub>3</sub>PdS<sub>4</sub>: C, 27.03 (26.56); H, 2.27 (2.32); S, 18.04 (17.85) %.

**Syntheses of compound  $\{[K_2(\mu-H_2O)_2(thf)_6][Pt(SC_6H_2Cl_2S)_2]\}_n$  (**3**).** This synthesis was carried out following the above procedure but using K<sub>2</sub>PtCl<sub>4</sub>. In this case the reaction time was increased up to 3.5 h. Suitable crystals for X-ray analysis of compound **3** (220 mg, 52.7 %) together with trace amounts of  $\{[K_2(\mu-H_2O)_2(\mu-thf)_2][Pt(SC_6H_2Cl_2S)_2]\}_n$  (**4**) were obtained from a solution of wet thf/*n*-heptane at -20 °C. Anal. Calcd. (Found) for **3**: C<sub>28</sub>H<sub>40</sub>Cl<sub>4</sub>K<sub>2</sub>O<sub>6</sub>PtS<sub>4</sub>: C, 33.10 (32.53); H, 3.97 (4.10); S, 12.62 (11.75) %.

## Conclusions

We have synthesized and investigated a series of bis-dithiolene coordination polymers based on group 10 metals linked by potassium complexes. Their structures show a common square-planar [M(SC<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>S)<sub>2</sub>]<sub>2</sub> moiety [M = Ni (**1**), Pd (**2**) and Pt (**3** and **4**)] but the supramolecular network organization is markedly influenced by the potassium coordination environment which is very sensitive to the coordination oxygen donor ligands, such as water or thf, therefore providing structures with different

dimensionalities. To our knowledge these compounds represent the first samples of 2D-CP networks containing group 10 metal dithiolene groups. These CPs show similar physical properties, they are diamagnetic and relatively good semiconductors.

In summary this work demonstrates that the combination of group 10 metal dithiolene entities with alkaline complexes allows the formation of coordination polymers with different novel architectures promoted by the coordination versatility of the alkaline metal centre. These materials show interesting electronic properties.

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