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# Facile synthesis of potassium tetrathiooxalate — The "true" monomer for the preparation of electron-conductive poly(nickel-ethylenetetrathiolate)



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# ABSTRACT

Herein, aiming at optimization of the polymerization process leading to a family of hole- and electronconducting 1,1,2,2-ethenetetrathiolate-based polymers, such as poly(nickel-1,1,2,2-ethenetetrathiolate), poly[K<sub>x</sub>(Ni-ett)], we investigated transformations of the monomer precursor 1,3,4,6-tetrathiapentalene-2,5-dione (TPD) occurring under polymerization conditions. We found that only one ring of TPD opens upon its reaction with potassium methoxide under inert conditions at room temperature which leads to the formation of potassium 2-oxo-1,3-dithiol-4,5-dithiolate (K<sub>2</sub>[**3**]). Heating of K<sub>2</sub>[**3**] under reflux in methanol solution under inert conditions opens the second ring, however the resulting product is not potassium ethenetetrathiolate (K<sub>4</sub>[**2**]), the product of an exhaustive methanolysis of TPD, but potassium tetrathiooxalate (K<sub>2</sub>[**4**]), the product of the decarbonylation of K<sub>2</sub>[**3**]. Preliminary experiments reveal that the involvement of K<sub>2</sub>[**4**] in the polymerization process is beneficial for reproducible formation of high quality 1,1,2,2-ethenetetrathiolate-based polymers suitable for thermoelectric applications.

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#### 1. Introduction

Potassium poly(nickel-1,1,2,2-ethenetetrathiolate), poly[K<sub>x</sub>(Niett)], after the first report of its synthesis in 1983 by Poleschner et al.,<sup>1</sup> had been thoroughly studied due to its extraordinary conductive properties. Though the investigations of different metal-organic complexes are steadily continuing in order to find materials for optical and electronic devices,<sup>2</sup> the second wave of interest to the poly[K<sub>x</sub>(Ni-ett)] arose in 2012 after the work of Sun et al.,<sup>3</sup> in which thermoelectric (TE) properties of the polymer were in detail investigated and an all-organic TE device with very promising characteristics was fabricated. Very recently, poly[K<sub>x</sub>(Niett)]-films with even more improved properties were obtained by an electrochemical method which provided a significant prospect

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of this polymer in the field of organic electronics.<sup>4</sup> However, a serious drawback of poly[K<sub>x</sub>(Ni-ett)] is its insolubility which poses severe difficulties in its processability (and fabrication of optoelectronic devices) and causes irreproducibility of its properties. While the former problem can partially be solved by the formulation of printable polymer-based composites by blending the polymer with various dispersants, 5-7 the latter issue still needs to be circumvented. Indeed, the formation of insoluble aggregates at early stages of the polymerization process limits the polymer crystallinity and complicates the purification process. As low solubility is an intrinsic property of poly[K<sub>x</sub>(Ni-ett)], a viable way to better control the polymer crystallinity and purity is to grow more ordered and pure structures directly during the polymer synthesis. For example, highly crystalline films of a structurally-related cobalt dithiolene-based polymer were recently fabricated by precise control over the mixing process of respective monomers.<sup>8</sup> However, the implementation of this approach in the case of poly[K<sub>x</sub>(Niett)] is problematic because of a very complex polymerization mechanism. Particularly, the concentration of the "true monomer"

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in the polymerization mixture is difficult to control because its formation involves a multi-step, yet poorly understood reaction of the monomer precursor 1,3,4,6- tetrathiapentalene-2,5-dione (TPD, **1**) and potassium methoxide. It is still not clear whether the eth-ylenetetrathiolate anion ( $2^{4-}$ ), which is considered in many previous works to be the "true monomer", is formed prior to the addition of nickel(II) chloride (which acts as a comonomer, Scheme 1, route A), or it forms during the polymerization (route B). It was particularly proposed that only one ring opens during the reaction of TPD with potassium methoxide to form potassium dithiolate ( $3^{2-}$ )(also known as dmid-<sup>9,10</sup> or dmio-ligand,<sup>11</sup> route B),<sup>4,12,13</sup> whereas the opening of the second ring is precluded by strong Coulomb repulsions between like-charged dithiolate and methoxide anions (such as occurring in route A).

Sun et al.<sup>4</sup> recently proposed that opening of the second ring requires the charge neutralization of dithiolate anion  $3^{2-}$ . It can occur either upon interaction with oppositely charged Ni<sup>2+</sup> or by oxidation of the dithiolate anion (route C) or similar species (for example, dianion [Ni(dmid)<sub>2</sub>]<sup>2-</sup>). The assumption that oxidation plays an important role in the polymerization process is supported

by the fact that the stoichiometry of the resulting polymer is far from a theoretical one (corresponding to the formula poly[K<sub>2</sub>(Niett)]), which can be expected for polymerizations of K<sub>4</sub>[**2**]and Ni(II) salts. In reality, the resulting polymer has a variable quantity of potassium and the most useful optoelectronic properties have polymers of the general formula poly[K<sub>x</sub>(Ni-ett)] with x ranging between 0.3 and 0.6. However, it can be alternatively proposed that the polymer with the observed stoichiometry is formed from a mixture of tetraanion **2**<sup>4-</sup> and dianion **4**<sup>2-</sup> rather than from **2**<sup>4-</sup> exclusively (combination of routes A-C). The present works aims to shed more light on the polymerization process and subsequently enabling possibilities for improvement.

#### 2. Results and discussion

#### 2.1. Structure of the monomer

The usual procedure for the  $poly[K_x(Ni-ett)]$  preparation includes a prolonged refluxing of TPD with potassium methoxide followed by the addition of nickel(II) chloride. We firstly wanted to



itemized route B:



Scheme 1. Possible routes of poly[K<sub>x</sub>(Ni-ett)] formation.

verify whether the heating and the base excess is necessary for the opening of both TPD rings. To this end, the reaction of TPD with an excess of potassium methoxide in deuterated methanol was monitored by <sup>13</sup>C NMR spectroscopy at room temperature and it indicated unambiguously the formation of anion **3**<sup>2–</sup> as the only sulfur-containing reaction product (Scheme 1) besides dimethyl carbonate as second reaction product. This was concluded from the disappearance of the TPD signals at  $\delta = 192.0$  ppm and  $\delta = 113.2$  ppm, which are assigned to the C=C double bond and the carbonyl group, respectively (SI, Fig. S1). The appearance of new signals at  $\delta = 198.9$  ppm and  $\delta = 125.4$  ppm (SI, Fig. S2) coincides with signals of analogous sodium salt of the **3**<sup>2–</sup> anion.<sup>14</sup>

Our in situ <sup>13</sup>C NMR experiments reveal that dianion  $3^{2-}$  forms immediately after mixing of the educts at room temperature. Dianion  $3^{2-}$  is stable in methanol solution under inert environment for at least one week when stirred at room temperature. Moreover, we have observed that the base excess has no influence on the reaction result. Only signals resulting from dianion  $3^{2-}$  are observed in the <sup>13</sup>C NMR spectra when 2, 4.6 or 12 equivalents of KOMe are used in the reaction. As such, our data show that only one ring opens in TPD at room temperature independent of the reaction time and stoichiometry of the base. It was proposed that strong electrostatic repulsions between negatively charged methoxide and dianion  $3^{2-}$ prevent the opening of the second ring of TPD. On the other hand, it is known that a high quality poly[K<sub>x</sub>(Ni-ett)] polymer is formed upon prolonged heating of TPD in the presence of the base and NiCl<sub>2</sub> suggesting the full ring opening of TPD under these conditions. Thus, it is to be questioned what exactly causes the full ring opening of TPD under polymerization conditions.

Two hypotheses were proposed in literature to explain this process. According to the first assumption, the added Ni(II) salts serve as the charge compensating agent so that the elementary polymerization cycle may include the following sequence: i) the opening of the first ring of the bicyclic TPD *via* methanolysis leads to doubly charged anion  $3^{2-}$  which is inactive to further methanolysis; ii) the reaction of anion  $3^{2-}$  with Ni(II) cations leads to charge neutralized intermediates; iii) the opening of anion  $3^{2-}$  by reaction with another equivalent of potassium methoxide. According to that mechanism, the resulting polymerization product should have the formula poly[K<sub>2</sub>(Ni-ett)] where each repeating unit of the backbone bears two negative charges (route B). However, the experimentally observed K/Ni ratio for the product is usually in the range of 0.6–0.3 which is much lower than the theoretically predicted K/Ni ratio of 2.

The unintended oxidation of the dianion (bis(1,3-dithiol-2-one-4,5-dithiolate)nickel) to the species with a lower degree of charge by air was proposed as an alternative hypothesis to explain the observed stoichiometry and, as the process facilitating the final ring opening *via* the formation of electrostatically neutral intermediate.<sup>4</sup> However, how the rather large amount of oxygen entered into the reaction mixture (when the mixture is not exposed to the air deliberately) and what the influence of the prolonged heating for the successful polymerization is were never verified experimentally so far.

In order to shed more light on these issues, we monitored transformations of  $K_2[3]$  at elevated temperature. To disentangle the roles of temperature, the oxidation process and the presence of Ni(II) salts and to disclose the final ring opening of  $3^{2-}$ , an addition experiment concerning the thermolysis of  $K_2[3]$  was conducted under inert conditions in the absence of nickel salts. Since even trace amounts of oxygen may play a critical role in this process, the reaction was carried out in exceptionally clean environment – in glovebox with oxygen level <0.1 ppm. Quite surprisingly, it was found that refluxing of a  $K_2[3]$  solution in the glovebox in methanolate leads to a complete decarbonylation

accompanied by the formation of a red-colored crystalline product which precipitated from the reaction mixture. The product shows only one signal in the <sup>13</sup>C NMR spectrum at  $\delta$  = 268.8 ppm (SI, Fig. S3) and was assigned to potassium tetrathiooxalate (K<sub>2</sub>[**4**]) by comparison with the literature data<sup>15</sup> and its structure was further verified by ESI-MS, IR measurements (SI) and X-ray crystal structure analysis (*vide infra*).

Only small amounts of other reaction compounds (unknown intermediates or side products) were found highlighting a high selectivity of the decarbonylation reaction. While reflux for 30 min leads to only a partial conversion of starting  $K_2[3]$  to product ( $K_2[4]$ ) (SI, Fig. S4), almost full conversion of  $K_2[3]$  was observed within 3 h under refluxing condition in methanol. Although the decarbonylation of  $K_2[3]$  was not described in the literature so far, the dimethyl derivative 4,5-bis(methylthio)-1,3-dithiol-2-one can be decarbonylated into the dimethyl tetrathiooxalate under photochemical<sup>16</sup> or pyrolytic<sup>17</sup> conditions. This may confirm indirectly the general feasibility of the transformation discovered in our work.

To elucidate a possible role of oxygen, the same reaction was conducted in the presence of air. This reaction resulted into a black colored mixture which contains a number of unknown products. Darkening of the reaction mixture was observed even faster in a vessel exposed to air at ambient atmosphere. Hence, the oxidationbased route C is unlikely a useful process during the polymerization although we do not exclude that some useful oxidations may proceed during the recovery/purification of the polymer from the reaction mixture (such as changes of the redox state of Ni atoms). It is noteworthy that the elimination of the carbon monoxide from  $K_{2}[\mathbf{3}]$  can be regarded as a redox reaction (disproportionation) as it resulted in CO (product of reduction) and accompanied by the oxidation of two carbons of double C=C-bond into carboxylic acid derivative resulting in the dianion  $\mathbf{4}^{2-}$  rather than in the tetraanion  $2^{4-}$ , the product of a hypothetical complete methanolysis of TPD. As such, this reaction explains the formation of formally oxidized product under anaerobic conditions. Furthermore, these experiments show that full ring opening of TPD may occur via route D, i.e., without the charge-compensating assistance of Ni(II) salts (route B); however, in the presence of Ni(II) salts route B may also be operative.

It should be emphasized that if the formation of poly[K<sub>x</sub>(Ni-ett)] under standard polymerization conditions proceeds exclusively through the polymerization of tetrathiooxalate dianion  $4^{2-}$  (route D), it should lead to the polymer poly[Ni-tto] (tto - tetrathiooxalate) having a completely uncharged backbone and no appreciable amounts of potassium ions. Since this is not the case, we suggest that both mechanisms, route B and D, are operative with varying contributions depending on the particular reaction conditions. However in all cases, route D dominates, because the usually observed content of K in poly[K<sub>x</sub>(Ni-ett)] is x = 0.3-0.6, which is closer to the theoretical content of K inherent to route D (x = 0) than to those of route B (x = 2).

It is also important to emphasize that although all routes should result in the conductive polymer, we intuitively suggest that route D, which involves the "true monomer", (compound  $K_2[4]$ ) rather than the monomer precursor (TPD) should provide more options for optimization of reaction conditions toward the synthesis of polymers with improved properties (e.g. higher purity, higher molecular weight, better crystallinity). Though our X-ray crystal structure analysis revealed that the anion [4] adopt a non-planar structure, ability of this ligand to make planar Ni(II) complexes with conducting properties was shown.<sup>18</sup> In earlier work Reynolds et al. reported the synthesis of highly conductive oligomers from the tetraethylammonium salt of tetrathiooxalate and Ni(OAc)<sub>2</sub>.<sup>19</sup> Along these lines, our preliminary experiments demonstrated that  $K_2[4]$  smoothly polymerizes in the presence of Ni(II) salts already at room temperature. Detailed investigation of this polymerization as well as of properties of the resulting polymer will be addressed in an ensuing work.

## 2.2. Crystals of potassium tetrathiooxalate (K<sub>2</sub>[4])

Tetrathiooxalate dianion  $\mathbf{4}^{2-}$  as a bidentate ligand is a structural fragment of a large number of compounds, which were isolated in pure form and characterized by X-ray analysis; however, salts with small cations are known mostly in solutions. Recently, potassium tetrathiooxalate was characterized as a complex with 18-crown-6 or DMSO.<sup>20</sup> Potassium tetrathiooxalate in the solid state was obtained as a yellowish-grey crude product,<sup>21,22</sup> but no structural characterizations were reported. While tetrathiooxalate salts with voluminous cations (Et<sub>4</sub> $N^+$ , Me<sub>4</sub> $N^+$  or Ph<sub>4</sub> $P^+$ ) are well-known, isolation of similar salts with smaller cations is difficult. It was suggested that a decrease of the cation size increases the tendency to form ion pairs, which limits the resonance stabilization in the dithiocarboxylate group.<sup>23</sup> From these assumptions, the isolation of tetrathiooxalate salts having relatively small potassium counterions is quite surprising. To unambiguously prove the formation of  $4^{2-}$ , we performed an X-ray crystallography analysis. Dark-red crystals of K<sub>2</sub>[4], suitable for X-ray diffraction studies were grown by crystallization from super-saturated solution of methanol.

**Crystal Data** for K<sub>2</sub>[**4**] (M = 230.46 g/mol): monoclinic, space group  $P_{21}/c$  (no. 14), a = 6.6421(4) Å, b = 10.8782(6) Å, c = 10.6814(6) Å,  $\beta = 99.919(5)^\circ$ , V = 760.23(8) Å<sup>3</sup>, Z = 4, T = 100.00(11) K,  $\mu$ (MoK $\alpha$ ) = 2.237 mm<sup>-1</sup>,  $\rho_{calc} = 2.014$  g/cm<sup>3</sup>, 3755 reflections measured ( $5.386^\circ \le 2\Theta \le 54.958^\circ$ ), 1744 unique ( $R_{int} = 0.0140$ ,  $R_{sigma} = 0.0206$ ) which were used in all calculations. The final  $R_1$  was 0.0181 (I >  $2\sigma$ (I)) and w $R_2$  was 0.0422 (all data).

The asymmetric unit of  $K_2C_2S_4$  is presented in Fig. 1a. Cations and anions form a three dimensional network. The  $4^{2-}$  coordinates two K<sup>+</sup> cations in several binding modes with S–K bond lengths ranging from 3.1249(5) Å (K1–S1) to 3.8560(5) Å (K1–S4'). The coordination environment around potassium can be seen in Fig. 1b and c. K1 is surrounded by nine sulfur atoms of four tetrathiooxalate ligands. One ligand coordinates *via* three sulfur atoms and three ligands are in bidentate coordination mode forming two fourmembered rings and one five membered ring. K2 is coordinated by nine sulfur atoms of five different anions. Two ligands are chelating forming five membered rings. Two ligands coordinate by only one thiolate group and one ligand donates *via* three sulfur atoms.

The non-planar  $C_2S_4^{2-}$  moiety is therefore surrounded by nine

K<sup>+</sup> cations. With a S2-C1-C2-S3 torsion angle of 79.30(11)° the two CS<sub>2</sub> units are almost orthogonal. Similar values are also found in the related structures of  $\{[K(18c6)]_2C_2S_4\}Py$ ,<sup>20</sup> [PPh4]<sub>2</sub>[C<sub>2</sub>S<sub>4</sub>]<sup>21</sup> and [NEt<sub>4</sub>]<sub>2</sub>[C<sub>2</sub>S<sub>4</sub>].<sup>24</sup> The C–C and C–S bond lengths (C1–C2 1.4969(17) Å, S1–C1 1.6795(13) Å and S2–C1 1.6905(13) Å, S3–C2 1.6739(12) Å and S4–C2 1.6930(13) Å) are in accordance with the other structures.

#### 3. Conclusion

In conclusion, we found that only one ring of TPD opens upon its reaction with potassium methoxide under inert conditions at room temperature which leads to the formation of potassium 2-oxo-1,3dithiol-4,5-dithiolate. Heating of the obtained methanol solution under reflux opens the second ring; however the resulting product is not potassium ethenetetrathiolate, the product of an exhaustive methanolysis of TPD, which is believed to be a "true monomer" for the synthesis of ethenetetrathiolate-based polymers, but potassium tetrathiooxalate. This compound was isolated as red crystals and its identity was proved by a single-crystal X-ray diffraction analysis. Potassium tetrathiooxalate smoothly polymerizes in the presence of Ni(II) salts confirming that it is the key intermediate in the synthesis of 1,1,2,2-ethenetetrathiolate-based polymers. We believe that the additional involvement of potassium tetrathiooxalate in the polymerization will help for the optimization of the polymerization process and lead to more reproducible preparation of high quality 1,1,2,2-ethenetetrathiolate-based polymers for thermoelectric applications.

#### 4. Experimental

#### 4.1. Chemicals

1,3,4,6-Tetrathiapentalene-2,5-dione (TCI-Europe), potassium methoxide (Sigma Aldrich), methanol (Carl Roth), MeOH- $d_4$  and DMF- $d_7$  (Euriso-Top) are used as received.

#### 4.2. Characterization techniques

<sup>13</sup>C (125 MHz) NMR spectra were recorded on a Bruker Avance III 500 spectrometer. Chemical shifts are reported in ppm with a solvent peak as an internal reference (MeOH-d<sub>4</sub>:  $\delta$  = 49.0 ppm; DMF-d<sub>7</sub>:  $\delta$  = 30.1 ppm). Single crystals of K<sub>2</sub>[**3**] were collected. A suitable crystal was selected and mounted in paraffin oil on a nylon



S2

Fig. 1. The crystal structure of K<sub>2</sub>[4] crystallized from methanol. (a) Asymmetric unit; Coordination environment around K1 (b) and K2 (c). Atoms labeled with ' are generated by symmetry. Ellipsoids in (a) are drawn at 90% probability level.

loop on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 100.00(11) K during data collection. Using Olex2,<sup>25</sup> the structure was solved with the ShelXT<sup>26</sup> structure solution program using Direct Methods and refined with the ShelXL<sup>27</sup> refinement package using Least Squares minimization. Fig. 1 was generated using Olex2.<sup>25</sup>

### 4.3. Syntheses

All reactions were carried out under an inert atmosphere using a Mbraun glovebox with a purifier unit, unless otherwise indicated.

#### 4.3.1. Potassium 2-oxo-1,3-dithiol-4,5-dithiolate $(K_2[3])$

To a solution of 1.557 g (22.2 mmol; 4.6 equivalents) of potassium methoxide dissolved in 20 ml methanol was added 1.0 g of 1,3,4,6-tetrathiapentalene-2,5-dione (4.8 mmol). The mixture was agitated with a magnetic stirrer for 20 min and then used for the synthesis of K<sub>2</sub>[4] (see below) or was kept standing at room temperature. In the last case yellow crystals were precipitated after 1 day, separated by filtration and washed with methanol and ether (1.015 g, 82%). <sup>13</sup>C NMR (MeOH-d<sub>4</sub>):  $\delta$  (ppm) 198.9 (C=O), 125.4 (C=C).

#### 4.3.2. Potassium tetrathiooxalate $(K_2[\mathbf{4}])$

The abovementioned solution (see the synthesis of  $K_2[3]$ ) was refluxed for 3 h, and then excess of solvent was distilled off. The precipitate was then filtered off and washed with diethyl ether. The vield is 80% (0.883 g) based on the 1.3.4.6-tetrathiapentalene-2.5dione. Crystals suitable for X-ray investigation were obtained by recrystallization of the crude product from methanol giving red parallelepipeds. <sup>13</sup>C NMR (MeOH-d<sub>4</sub>):  $\delta$  (ppm) 269.8.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.tet.2017.03.010.

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