



## Bisdithiolene complexes based on an extended ligand with TTF and pyridine moieties

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### ABSTRACT

The synthesis and characterization of a new extended tetrathiafulvalene (TTF) dithiolene ligand substituted with alkyl pyridine groups, pyridylethylsulfanyl-tetrathiafulvalenedithiolene (pesdt<sup>2-</sup>), as well as the corresponding gold (III) complex [Au(pesdt)<sub>2</sub>]<sup>-</sup> obtained as a tetrabutylammonium salt are described. The oxidation potential of this complex is rather low and the paramagnetic neutral complex is obtained as an electrically insulating microcrystalline powder.

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Square planar neutral complexes with extended dithiolene ligands have attracted increasing interest due to their extended  $\pi$ -conjugation system and possibility of displaying high electrical conductivity [1]. A few nickel, copper and gold bisdithiolene complexes with extended TTF ligands exhibiting properties of metals in their neutral state have been reported, [2] as also found in not so extended dithiolene ligands [3]. In these metal complexes with extended TTF-dithiolene ligands, the side groups on the TTF moiety have been so far restricted to alkyl groups or conjugated rings. Another recent trend in dithiolene chemistry has been the incorporation of functional groups containing N atoms able to coordinate transition metals, in order to explore new coordination structures [4] relevant in the field of magnetic conductors or magnetic coordination polymers, as has already been described for some TTF type donors [5]. In this paper we describe the synthesis and characterization of the first pyridine substituted extended dithiolene ligand with TTF moieties and the corresponding gold complex.

The new TTF-based donor, 4,5-Bis(2-cyanoethylthio)-4',5'-Bis(2-pyridylethylsulfanyl)tetrathiafulvalene (**1**), is the precursor for the preparation of the dithiolene based on the pyridylethylsulfanyl-tetrathiafulvalene (pesdt) ligand, where the cyanoethyl group is used as a protecting group (Scheme 1). TTF derivative **1** was obtained by the cross-coupling reaction of 4,5-Bis(2-pyridylethylsulfanyl)-1,3-dithiol-2-one and 4,5-Bis(2'-cyanoethylthio)-1,3-dithiol-2-one in toluene in the presence of P(OEt)<sub>3</sub> [6]. This coupling reaction also gives rise to by-products resulting from the self-coupling of the reactants. It is, however, possible to obtain **1** in good yield, 48%, after column purification. X-ray quality single crystals were obtained from slowly

cooling a toluene solution. Fig. 1 shows an ORTEP plot of **1** with the atomic numbering scheme employed [7,8].

The central TTF core and thioether S atoms are essentially planar (Rms deviation of fitted atoms: 0.043 Å) while the ethyl-pyridine and cyanoethyl groups deviate from the central plane. One of the ethyl-pyridine and one of the cyanoethyl "arms" are disordered over two conformations with occupancies (0.509:0.491). The dihedral angles between the pyridine rings and the TTF mean plane are 86.5(1)° and 58.9(3)° or 66.28(3)°. Bond lengths and angles in the TTF moiety are in the range expected for neutral TTF derivatives [9]. The crystal structure is composed by head to head donor stacks along the *b* plane at variance with the usual packing motif of extended TTFs which is head to tail, so that one dithiole end of each molecule fills the intramolecular cavity of the other [10]. In the structure of **1** the cyanoethyl "arms" are segregated from the pyridine rings and no intermolecular short S...S contacts are found.

The synthesis of (*n*-Bu<sub>4</sub>N) [Au(pesdt)<sub>2</sub>] (**2**) was performed following general procedures for this type of complexes from **1** by means of hydrolytic cleavage with *n*-Bu<sub>4</sub>NOH in MeOH/THF under strictly inert atmosphere using Schlenk techniques [11]. The ligand generated was immediately reacted with KAuCl<sub>4</sub> and precipitated as an *n*-Bu<sub>4</sub>N salt. Recrystallization was possible from the slow diffusion of diisopropyl ether into a solution of the complex in dichloromethane. Elemental analysis indicates a cation to anion 1:1 stoichiometry.

Although the quality of crystals obtained of compound **2** was poor and the structure refinement of low quality, mainly due to disorder in the ethyl-pyridine groups, it was possible to unambiguously identify its molecular structure and crystal packing [7,12]. The molecular structure of the gold complex in **2** is shown in Fig. 2. The metal complex presents an almost perfect square planar coordination geometry with Au-S bond lengths typical of Au<sup>III</sup> and the central sulfur rich core essentially planar. The ethyl-pyridine groups present severe disorder

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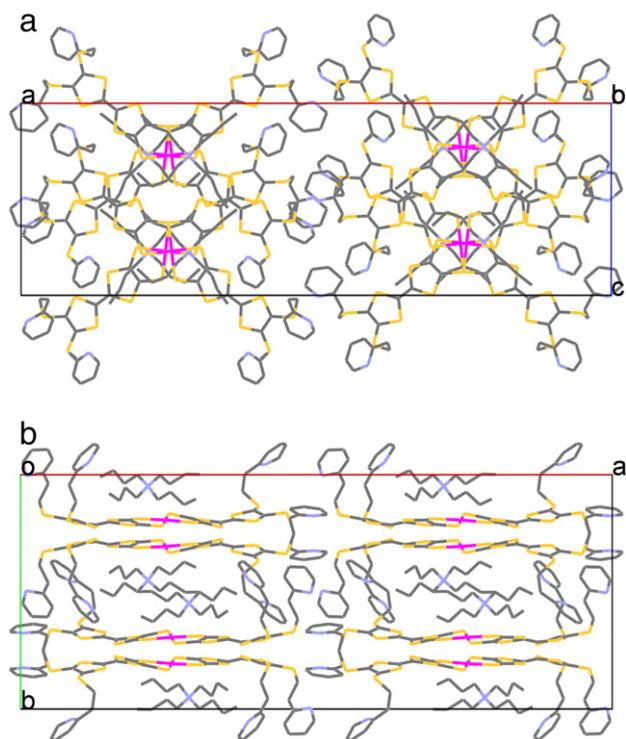


Fig. 3. Crystal packing of compound **2** viewed along (a) *b* and (b) *c*.

pyridine groups are expected to be relevant as key building blocks to prepare magnetic conductors and magnetic coordination structures.

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### Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC – 753529 for **1** and CCDC – 754683 for **2**). Copies of this information

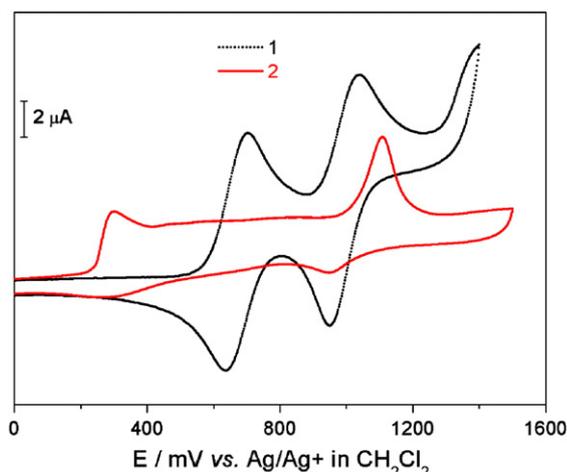


Fig. 4. Cyclic voltammograms of TTF derivative **1** and complex **2**.

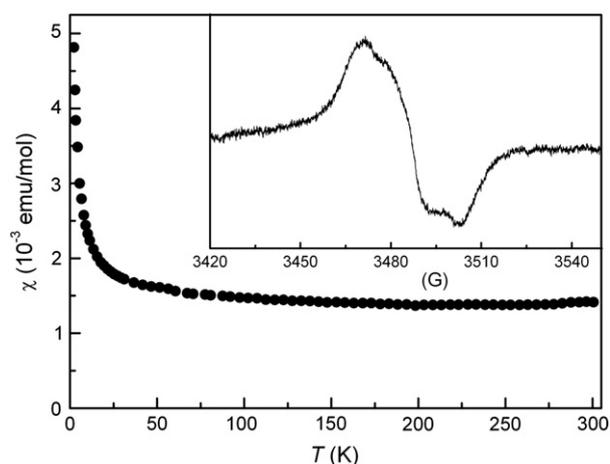


Fig. 5. Paramagnetic susceptibility vs temperature plot for complex **3**. The inset shows the room temperature EPR spectrum of a powder sample.

can be obtained free of charge from [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

Supplementary data associated with this article, including tables of selected bond lengths (Å) and angles (°) of TTF **1** and complex **2**, figure showing the atomic numbering scheme of **2** and the effective magnetic moment vs temperature plot for complex **3** can be found in the online version, at [doi:10.1016/j.inoche.2011.10.001](https://doi.org/10.1016/j.inoche.2011.10.001).

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- [7] 4,5-Bis(2-pyridylethylsulfanyl)-1,3-dithiol-2-one (4.80 g, 12.5 mmol) and 4,5-Bis(2'-cyanoethylthio)-1,3-dithiol-2-one [18] (3.60 g, 12.5 mmol) were dissolved in dried toluene (100 mL) under N<sub>2</sub>. The solution was heated under reflux before the addition of dried P(OEt)<sub>3</sub> (10 mL). This solution was left at reflux overnight under N<sub>2</sub>. After cooling to room temperature, the orange precipitate was collected by filtration. The filtrate was evaporated, and column chromatography on silica gel with EtOAc/Hex 8:2 afforded **1** (4.0 g, 6.0 mmol). X-ray quality crystals were obtained from the slow evaporation of a toluene solution. Yield: 48%; m. p. 118 °C; C<sub>26</sub>H<sub>24</sub>N<sub>4</sub>S<sub>8</sub> (648.97): calcd. C 48.14, H 3.70, N 8.64, S 39.50%; found C 48.67, H 3.20, N 8.66, S 39.74%; LDI(+) M<sup>+</sup><sub>calcd</sub> = 647.97611; M<sup>+</sup><sub>found</sub> = 647.98312 (37%);

- $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  = 8.55 (dd,  $J$  = 4.7 Hz, 2H, 6-H), 7.62 (dt,  $J$  = 8.2, 6.4 Hz, 2H, 4-H), 7.17 (m, 4H, 3-H, 5-H), 3.25 (t,  $J$  = 7.6, 6.4 Hz, 2H,  $\text{CH}_2$ ), 3.11 (m, 4H,  $\text{CH}_2$ ), 2.76 (t,  $J$  = 7.6, 6.4 Hz, 2H,  $\text{CH}_2$ ) ppm;  $^{13}\text{C}$  NMR (75.3 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  = 158.8, 149.5, 149.4, 136.6, 128.1, 128.0, 123.5, 121.8, 117.5, 114.7, 107.5, 38.2, 35.8, 35.6, 31.2, 18.9 ppm.
- [7] The data were collected on a Bruker AXP APEX CCD area detector diffractometer equipped with an Oxford Cryosystems low temperature device at 150(2) K in the  $\omega$  and  $\phi$  scans mode. A semi-empirical absorption correction was carried out using the program SADABS [19]. Data collection, cell refinement and data reduction were done with the SMART and SAINT programs [20]. The structure was solved by direct methods using SIR97 [21] and refined by full-matrix least-squares methods with SHELXL97 [22] program using the winGX software package [23].
- [8] The crystal data and structural parameters for **1**:  $\text{C}_{26}\text{H}_{24}\text{N}_4\text{S}_8$ ,  $M_r$  = 648.97, Monoclinic, space group  $P2_1/c$ ,  $a$  = 31.256(2) Å,  $b$  = 5.1072(3) Å,  $c$  = 18.6504(12) Å,  $\beta$  = 103.432(3)°,  $V$  = 2895.8(3) Å<sup>3</sup>,  $Z$  = 4,  $D_c$  = 1.489 mg/m<sup>3</sup>,  $\mu$  = 0.642 mm<sup>-1</sup>, GOF = 0.949. A total of 8921 reflections were collected and 5268 are unique ( $R_{\text{int}}$  = 0.0489),  $R1$  ( $wR2$ ) = 0.0481 (0.0954).
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- [11] (*n*-Bu<sub>4</sub>N) [Au<sup>III</sup>(pesdt)<sub>2</sub>] (**2**): TTF derivative **1** (0.45 g, 0.70 mmol) was dissolved in dry THF (6 mL) and the temperature was lowered to –78 °C under N<sub>2</sub>, before slow addition of a solution of *n*-Bu<sub>4</sub>NOH 0.1 M in MeOH (30 mL). After 10 min. the solution was allowed to slowly reach room temperature, after which it was further stirred for 3 h. The solution was then cooled down to –78 °C and KAuCl<sub>4</sub> (0.134 g, 0.35 mmol) in MeOH (9 mL) was added dropwise. The solution was allowed to slowly reach room temperature overnight. The precipitate was filtered, washed with MeOH (3 × 10 mL), Et<sub>2</sub>O (2 × 10 mL) and dried under vacuum. Yield: 57%; m. p. 117–118 °C;  $\text{C}_{56}\text{H}_{67}\text{AuN}_5\text{S}_{16}$  (1520.2); calcd. C 44.24, H 4.44, N 4.61%; found C 44.23, H 4.75, N 4.62%; LDI(–)  $M^+$  calcd = 1276.8;  $M^+$  found = 1276.9 (100%);  $M^+$  found = 242.1 (100%);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  = 8.51 (d,  $J$  = 4.7 Hz, 2H, 6-H), 7.59 (dt,  $J$  = 1.7, 7.6 Hz, 2H, 4-H), 7.19 (d,  $J$  = 7.6 Hz, 2H, 3-H), 7.12 (dt,  $J$  = 1.7, 7.6 Hz, 2H, 5-H), 3.22 (t,  $J$  = 7.6 Hz, 4H,  $\text{CH}_2$ ), 3.09 (t,  $J$  = 7.6 Hz, 4H,  $\text{CH}_2$ ), 1.62 (m, 8H,  $\text{CH}_2$ ), 1.50 (q, 8H,  $\text{CH}_2$ ), 1.02 (t,  $J$  = 7.0 Hz, 8H,  $\text{CH}_2$ ) ppm.
- [12] The crystal data and structural parameters for **2**:  $\text{C}_{56}\text{H}_{68}\text{AuN}_5\text{S}_{16}$ ,  $M_r$  = 1521.08, Orthorhombic, space group  $Pbca$ ,  $a$  = 46.185(9) Å,  $b$  = 18.337(3) Å,  $c$  = 15.056(2) Å, and  $V$  = 12751(4) Å<sup>3</sup>.  $Z$  = 8,  $D_c$  = 1.585 mg/m<sup>3</sup>,  $\mu$  = 2.873 mm<sup>-1</sup>, GOF = 1.185. A total of 76138 reflections were collected and 6714 are unique ( $R_{\text{int}}$  = 0.1796),  $R1$  ( $wR2$ ) = 0.1756 (0.3685).
- [13] [Au<sup>IV</sup>(pesdt)<sub>2</sub>] (**3**): Neutral complex [Au(pesdt)<sub>2</sub>] was prepared by electrochemical oxidation of (*n*-Bu<sub>4</sub>N) [Au<sup>III</sup>(pesdt)<sub>2</sub>] at a constant current of 0.5 μA in dried  $\text{CH}_2\text{Cl}_2$  containing *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte at 20 °C. For all reaction condition, only powder samples were obtained.  $\text{C}_{40}\text{H}_{32}\text{AuN}_4\text{S}_{16}$  (1278): calcd. C 37.57, H 2.52, N 4.38%; found C 37.48, H 2.74, N 4.21%.
- [14] EPR spectra were obtained at room temperature on powder using a conventional in an X-Band Bruker ESP 300E spectrometer equipped with a microwave bridge ER041XK, a rectangular cavity operating in T102 mode and a field controller ER032M system. The modulation amplitude was kept significantly below the linewidth and the microwave power significantly below saturation.
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