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# Radical Cation Salts of Tetramethyl-tetrathiafulvalene (TM-TTF) and Tetramethyl-tetraselenafulvalene (TM-TSF) with Chlorocyananilate-based Anions

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**KEYWORDS.** TM-TTF, TM-TSF, anilate, chlorocyananilate, electrocrystallization, molecular conductors

**ABSTRACT:** Electrocrystallization of tetramethyl-tetrathiafulvalene (TM-TTF) and tetramethyl-tetraselenafulvalene (TM-TSF) with chlorocyananilate monoanion or/and tris(chlorocyananilato)ferrate(III) in THF/DCM solvent mixtures yielded a salt formulated as [TM-TTF]<sub>4</sub>[K(HClCNAn)<sub>4</sub>] (**1**) with the former, and  $\pi$ -d hybrid systems, formulated as [TM-TTF]<sub>5</sub>[Fe(ClCNAn)<sub>3</sub>](CH<sub>2</sub>Cl<sub>2</sub>)<sub>2</sub> (**2**) and [TM-TSF]<sub>3</sub>[Fe(ClCNAn)<sub>3</sub>](CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.5</sub>(H<sub>2</sub>O)<sub>2.5</sub> (**3**), respectively, with the later. Compound **1** shows segregation of TM-TTF donor molecules and K(HClCNAn)<sub>4</sub> anionic clusters in the *bc* plane. The donor molecules are present as mixed-valence dimers and show  $\beta'$  packing arrangement. Compounds **2** and **3** consist of hybrid organic/inorganic structures with no segregation of [Fe(ClCNAn)<sub>3</sub>]<sup>3-</sup> anionic complexes and organic TM-TTF/TM-TSF donors. In the structure of compound **3**, TM-TSF dimers are trapped between anilate units of metal complexes of opposite chirality. Furthermore, tetrameric donor motifs and crystallization solvent molecules complete the structure. Single-crystal conductivity measurements on compounds **1-2** show semiconducting behavior with room-temperature conductivity values of  $5 \times 10^{-5} \text{ S cm}^{-1}$  and  $2 \times 10^{-4} \text{ S cm}^{-1}$  and activation energies of 1960 K and 1900 K, respectively. Under high pressure, compound **2** remains semiconductor, yet its room-temperature conductivity value strongly increases up to  $0.2 \text{ S cm}^{-1}$  at 9.8 GPa.

## 1. INTRODUCTION

Molecular conductors have attracted special interest in material chemistry since the discovery of the first purely organic metallic conductor with TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) charge transfer salt and superconductivity behavior in the [TM-TSF]<sub>2</sub>[X] (TM-TSF = tetramethyl-tetraselenafulvalene, X = PF<sub>6</sub>, AsF<sub>6</sub>, SbF<sub>6</sub>, ClO<sub>4</sub>, etc.) series.<sup>1-4</sup> Subsequently, the closely related donor TM-TTF (tetramethyl-tetrathiafulvalene) was investigated in the [TM-TTF]<sub>2</sub>X (X = ClO<sub>4</sub>, PF<sub>6</sub>, AsF<sub>6</sub>,...) series, to investigate the role of the chalcogen atom in the crystal structures and transport properties of the corresponding compounds.<sup>5-9</sup> Thereafter, many other molecular conductors based on TTF and TSF derivatives have been studied, focusing on their transport properties (from metals to superconductors).<sup>10-15</sup> The functionalization of TTF moiety gives the possibility to tune the electronic properties of the donor molecules, promotes additional intermolecular interactions in the solid state and ultimately determines the physical properties of the molecular materials.<sup>16-18</sup>

Furthermore, by combining delocalized  $\pi$ -electrons with localized d-electrons, hybrid organic-inorganic  $\pi$ -d systems have been widely explored as a straightforward strategy to design multifunctional materials, where different physical properties coexist in the same crystal lattice.<sup>19,20</sup> A plethora of anions, ranging from simple mononuclear complexes like [MX<sub>4</sub>]<sup>n</sup> (M = Fe<sup>III</sup>, Cr<sup>III</sup>, Cu<sup>II</sup>; X = Cl

, Br<sup>-</sup>) to bimetallic layered coordination polymers, have been used in combination with TTF derivatives to provide magnetic conductors, such as (BEDT-TTF)<sub>4</sub>[(H<sub>3</sub>O)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·PhCN (BEDT-TTF = bis(ethylenedithio)-tetrathiafulvalene, C<sub>2</sub>O<sub>4</sub><sup>2-</sup> = oxalate), the first molecular paramagnetic superconductor,<sup>21</sup> κ-(BETS)<sub>2</sub>[FeBr<sub>4</sub>] (BETS = bis(ethylenedithio)tetraselenafulvalene), the first molecular antiferromagnetic superconductor,<sup>22,23</sup> and (BEDT-TTF)<sub>3</sub>[MnCr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>], the first molecular ferromagnetic metal.<sup>24</sup>

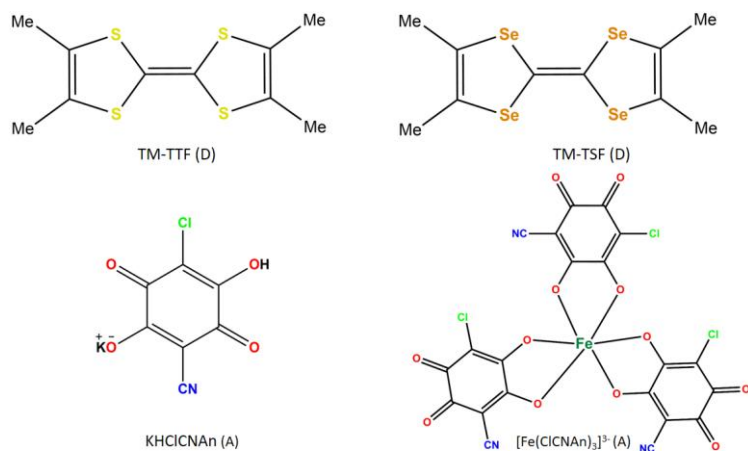
More often, it is generally observed that donor-anion stoichiometric ratio of 2:1 along with partially oxidised/mixed-valence oxidation state on donor molecules, yields high electrical conductivity.<sup>1-4</sup> However, radical cation salts with different donor:anion stoichiometric ratios, showing interesting conducting properties, are reported, such as (TMTSF)<sub>5</sub>[Cu(dcdmp)<sub>2</sub>]<sub>4</sub>, with a 5:4 donor:anion ratio, having an electrical conductivity σ<sub>RT</sub> of 134 S cm<sup>-1</sup>.<sup>10</sup>

Among the anions used so far,<sup>25-28</sup> 3,6-disubstituted-2,5-dihydroxy-1,4-benzoquinone, also known as anilates,<sup>29</sup> have attracted interest in the molecular conductors field thanks to their redox behavior and their versatility in changing the substituents (halogens, cyano, thiophene, etc.)<sup>30,31</sup> at the 3,6 positions of the anilato moiety, which can give rise to different intermolecular interactions.<sup>32-36</sup>

Additionally, anilate derivatives are interesting building blocks for the design of various multifunctional materials showing luminescence,<sup>37-40</sup> magnetism or/and conductivity.<sup>41-45</sup> Pioneer work with anilates, used as anions in charge transfer salts based on TTF derivatives, yielded organic conductors and Mott insulators by diffusing cyananilic acid with TM-TTF and BEDT-TTF, respectively.<sup>46-48</sup>

Recently, some of us have reported on purely organic and hybrid organic/inorganic compounds based on anilate derivatives with BEDT-TTF.<sup>33,34,36</sup> Accordingly, radical cation salts based on BEDT-TTF with chlorocyananilate (HCICNAn<sup>-</sup>) and chloranilate (HCl<sub>2</sub>An<sup>-</sup>), formulated as (BEDT-TTF)<sub>2</sub>(HCICNAn) and (BEDT-TTF)(HCl<sub>2</sub>An), respectively, contain mixed-valence oxidation state donors and show semiconducting behavior. In addition, magnetic conductors were obtained by combining BEDT-TTF with [Fe(X<sub>2</sub>An)]<sup>3-</sup> (X = Cl or Cl/CN), giving rise to π-d hybrid systems with different donor-anion stoichiometric ratios such as 3:1, 6:1, 4:1, 5:2, etc.<sup>33,34</sup>

In this work, the asymmetric chlorocyananilate ligand and its tris(chlorocyananilato)ferrate(III) complex have been used as counterions in electrocrystallization experiments with TM-TTF or/and TM-TSF (Chart 1), affording radical cation salts formulated as [TM-TTF]<sub>4</sub>[K(HCICNAn)<sub>4</sub>] (**1**), [TM-TTF]<sub>5</sub>[Fe(CICNAn)<sub>3</sub>]·(CH<sub>2</sub>Cl<sub>2</sub>)<sub>2</sub> (**2**) and [TM-TSF]<sub>3</sub>[Fe(CICNAn)<sub>3</sub>]·(CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.5</sub>(H<sub>2</sub>O)<sub>2.5</sub> (**3**). The latter represents the first example of radical cation salts based on TM-TSF and anilate derivatives. The thorough structural characterization of compounds **1-3**, with a special emphasis on the intermolecular interactions, along with their transport properties are discussed herein.



**Chart 1.** Structure of donors (D) and anions (A) used in this work.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials and Methods

KHCICNAn and  $(\text{PPh}_4)[\text{Fe}(\text{CICNAn})_3]$  was prepared according to the procedure described in literature.<sup>31</sup> TM-TTF and TM-TSF were commercially purchased. Crystals were obtained by using the electrocrystallization technique.

### 2.2 Synthetic Procedures

**[TM-TTF]<sub>4</sub>[K(HCICNAn)<sub>4</sub>] (1).** TM-TTF (0.0115 mmol) and KHCICNAn (0.0345 mmol) were dissolved in 2:1 THF/DCM solvent mixtures (7 mL each) and placed in the anodic and cathodic chambers of an H-cell respectively. Single crystals were obtained on the anodic electrode over a period of one week by applying 1  $\mu\text{A}$  current at 20 °C.

**[TM-TTF]<sub>5</sub>[Fe(CICNAn)<sub>3</sub>]•(CH<sub>2</sub>Cl<sub>2</sub>)<sub>2</sub> (2).** Crystals of compound **2** were grown using similar conditions as **1**, except that a  $(\text{PPh}_4)[\text{Fe}(\text{CICNAn})_3]$  solution (0.0115 mmol) was placed in the cathodic chamber instead of KHCICNAn.

**[TM-TSF]<sub>3</sub>[Fe(CICNAn)<sub>3</sub>]•(CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.5</sub>(H<sub>2</sub>O)<sub>2.5</sub> (3).** Crystals of compound **3** were grown using similar conditions as **2**, except that a TM-TSF solution (0.0115 mmol) was placed in the anodic chamber instead of TM-TTF.

### 2.3 Crystallography

Single-crystal X-Ray diffraction measurements were collected on Agilent Supernova diffractometer with Cu K $\alpha$  ( $\lambda = 1.54184 \text{ \AA}$ ) at 150 K. Single crystals of **1-3** were mounted on a glass fiber loop using a viscous hydrocarbon oil to coat the crystal and then transferred directly to the cold nitrogen stream for data collection. The structures were solved by direct methods with the SIR97 program and refined against all  $F^2$  values with the SHELXL-97 program using the WinGX graphical user interface. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined isotropically with a riding model. The structure of compound **3** was refined as a two-component twin. The program SQUEEZE from PLATON was used for **2** to calculate the potential solvent-accessible void volume. It has indicated a total void space of 867  $\text{\AA}^3$  and 339 electrons/cell. This corresponds to two molecules of dichloromethane (DCM) that have been inserted in the empirical formula. A summary of crystallographic data and structure refinement are listed in Table 1.

**Table 1.** Crystallographic data of compounds **1-3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	$\text{C}_{68}\text{H}_{52}\text{Cl}_4\text{KN}_4\text{O}_{16}\text{S}_{16}$	$\text{C}_{73}\text{H}_{64}\text{Cl}_7\text{FeN}_3\text{O}_{12}\text{S}_{20}$	$\text{C}_{51.50}\text{H}_{42}\text{Cl}_4\text{FeN}_3\text{O}_{14.50}\text{Se}_{12}$
Fw	1874.99	2120.47	2080.05
Crystal color	black	black	black
Crystal size (mm <sup>3</sup> )	0.08*0.06*0.03	0.22*0.03*0.02	0.18*0.11*0.04
Temperature (K)	150	150	290
Wavelength ( $\text{\AA}$ )	1.54184	1.54184	1.54184
Crystal system, Z	Triclinic, 1	Monoclinic, 4	Monoclinic, 4
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
a ( $\text{\AA}$ )	12.5420(5)	23.9176(11)	11.544(5)
b ( $\text{\AA}$ )	13.0121(6)	19.6509(10)	22.884(5)
c ( $\text{\AA}$ )	13.6523(7)	18.3141(9)	25.978(5)
$\alpha$	112.978(4)	90	90

$\beta$	105.478(4)	97.168(4)	95.474(5)
$\gamma$	97.397(4)	90	90
V (Å <sup>3</sup> )	1907.51(17)	8540.4(7)	6831(4)
$\rho_{\text{calc}}$ (g.cm <sup>-3</sup> )	1.632	1.649	2.022
$\mu(\text{CuK}\alpha)$ (mm <sup>-1</sup> )	6.584	8.517	11.040
$\theta$ range (°)	3.750-73.449	2.920-73.646	2.578-74.352
Data collected	14322	17357	15243
Data unique	7364	8305	15243
Data observed	5816	5420	12116
Number of parameters / restraints	547/17	507/19	802/26
R(int)	0.0451	0.0661	0.0705
R1(F), <sup>a</sup> I > 2 $\sigma$ (I)	0.0834	0.0909	0.0880
wR2(F2), <sup>b</sup> all data	0.2137	0.2738	0.2660
S(F2), <sup>c</sup> all data	1.088	0.999	1.038

$${}^a R1(F) = \sum ||F_0| - |F_c|| / \sum |F_0|; {}^b wR2(F^2) = [\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^4]^{1/2}; {}^c S(F^2) = [\sum w(F_0^2 - F_c^2)^2 / (n+r-p)]^{1/2}.$$

## 2.4 Single-Crystal Conductivity Measurements

Resistivity measurements were carried out on different single crystals of compounds **1** and **2** with the two contacts methods in the temperature range of 300–150 K. Measurements were performed on prismatic-shaped single crystals of compound **1**, and on needle-shaped single crystals of compound **2**. For compound **1**, two-probe DC measurements were performed under vacuum, applying a constant voltage of 1.5 V and measuring the current using a Keithley 6487 Picoammeter / Voltage Source. Low temperature was provided by a home-made cryostat equipped with a 4 K pulse-tube using a cernox in good thermal contact with the samples as thermometer. For compound **2**, a modified Diamond Anvil Cell (DAC) four-probe DC resistivity measurement technique was used for the high pressure measurements. Electrical contacts were obtained attaching four 10  $\mu\text{m}$  gold wires and gold paint on a single crystal size of  $0.13 \times 0.03 \times 0.02 \text{ mm}^3$ . The sample was encapsulated with a mixture of epoxy and alumina. A diamond anvil with culet size of 0.7 mm and tension annealed stainless steel SUS301 was used. Daphne Oil 7373 was used as the pressure transmitting medium. The pressure was determined by the shift of ruby fluorescence R1 lines at room temperature.

## 3. RESULTS AND DISCUSSION

### 3.1 Synthetic Procedures

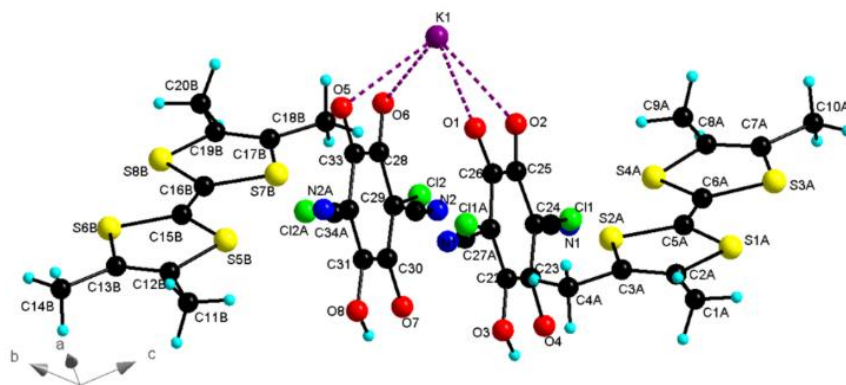
Electrocrystallization of TM-TTF and TM-TSF donors with potassium salt of monoprotonated chlorocyananilate (KHClCNAn) or/and tris(chlorocyananilato)ferrate(III) complex (PPh<sub>4</sub>)<sub>3</sub>[Fe(ClCNAn)<sub>3</sub>], in a THF/DCM mixture, yielded the radical cation salts [TM-TTF]<sub>4</sub>[K(HClCNAn)<sub>4</sub>] (**1**), [TM-TTF]<sub>5</sub>[Fe(ClCNAn)<sub>3</sub>] $\cdot$ (CH<sub>2</sub>Cl<sub>2</sub>)<sub>2</sub> (**2**) and [TM-TSF]<sub>3</sub>[Fe(ClCNAn)<sub>3</sub>] $\cdot$ (CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.5</sub>(H<sub>2</sub>O)<sub>2.5</sub> (**3**). The same experimental conditions were used except for the donor-anion stoichiometric ratios (1:3 for **1** and 1:1 for **2** and **3**, see Table 1). Attempts to electrocrystallize TM-TSF with KHClCNAn were unsuccessful so far.

**Table 2.** Precursors and synthetic conditions used for compounds **1-3**.

Experimental conditions: Solvent: THF/DCM; Current: 1 $\mu$ A			
Donors (D)/ Anions (A)	TM-TTF	TM-TSF	D:A ratios used
KHCICNAn	[TM-TTF] <sub>4</sub> [K(HCICNAn) <sub>4</sub> ] ( <b>1</b> )	-	1:3
[Fe(CICNAn) <sub>3</sub> ] <sup>+</sup>	[TM-TTF] <sub>5</sub> [Fe(CICNAn) <sub>3</sub> ] $\cdot$ (CH <sub>2</sub> Cl <sub>2</sub> ) <sub>2</sub> ( <b>2</b> )	[TM-TSF] <sub>3</sub> [Fe(CICNAn) <sub>3</sub> ] $\cdot$ (CH <sub>2</sub> Cl <sub>2</sub> ) <sub>0.5</sub> (H <sub>2</sub> O) <sub>2.5</sub> ( <b>3</b> )	1:1

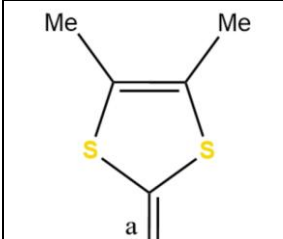
### 3.2 Solid-State Structures

Single-crystal X-ray studies show that compound **1** crystallizes in the triclinic *P*-1 space group, with two independent TM-TTF donor molecules (A and B), two HCICNAn<sup>-</sup> anions and half potassium cation K<sup>+</sup> in the asymmetric unit, leading to the formula [TM-TTF]<sub>4</sub>[K(HCICNAn)<sub>4</sub>] (Figure 1).

**Figure 1.** Asymmetric unit in the crystal structure of compound **1**.

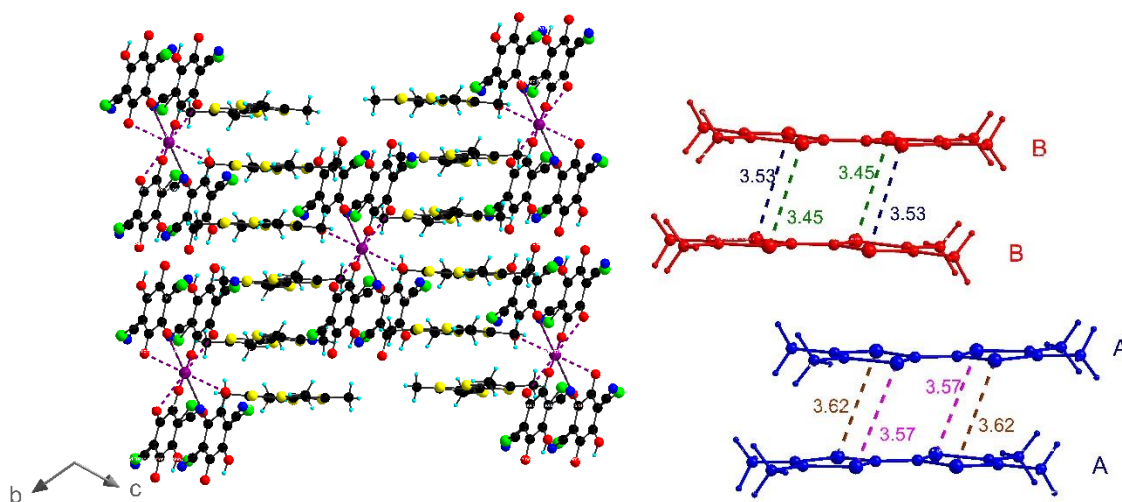
In the crystal packing, there is segregation between TM-TTF donor molecules and K(HCICNAn)<sub>4</sub> anionic clusters in the *bc* plane, where columns of donors alternate with columns of anions (Figure 2a). The central C=C and internal C-S bond lengths of the TM-TTF molecules indicate mixed valence oxidation state for donors. The charge is estimated by using two methods: i) bond length differences by tentatively applying the same empirical formula as for BEDT-TTF salts,  $Q = 6.347 - 7.4638 \cdot \delta^{49,50}$  and ii) bond distances ratio  $Q = -15.55 + 20.42 (a/b)^{51,52}$  (Table 3).

**Table 3.** Estimated charge calculation on TM-TTF donors in compound **1** by using average bond distances.

		<b>A</b>	<b>B</b>
	a	1.380(7)	1.387(8)
b	1.732(6)	1.713(6)	
	1.733(6)	1.708(6)	
	1.734(6)	1.711(6)	
	1.734(6)	1.718(6)	
c	1.757(7)	1.743(7)	
	1.745(6)	1.742(7)	

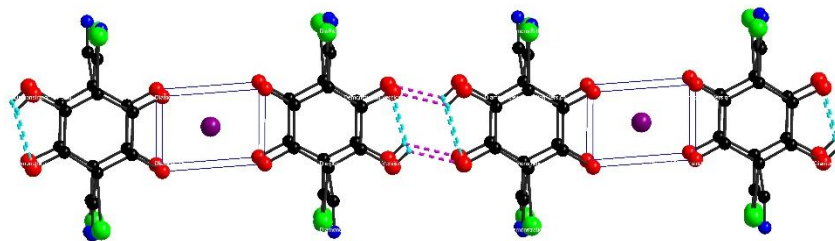
		1.759(7)	1.702(9)
		1.752(6)	1.746(9)
	d	1.337(11)	1.334(12)
		1.325(11)	1.340(15)
$\delta=(b+c)-(a+d)$	$\delta$	0.775	0.721
$Q=6.347-7.4638\cdot\delta^{49,50}$	<b>Q</b>	<b>0.56</b>	<b>0.96</b>
$r=a/b$	r	0.796	0.810
$Q=-15.55+20.42r^{51,52}$	<b>Q</b>	<b>0.7</b>	<b>0.99</b>

The organic donor layers are formed by alternated slipped dimers AA and BB in the *bc* plane, with short intermolecular S...S contacts (less than the sum of van der Waal radii 3.65 Å), favoring  $\beta'$  packing (Figure 2b, Figure S1-S2, ESI). Along the stack, the donor molecules are arranged in ...AABB... repeating units.



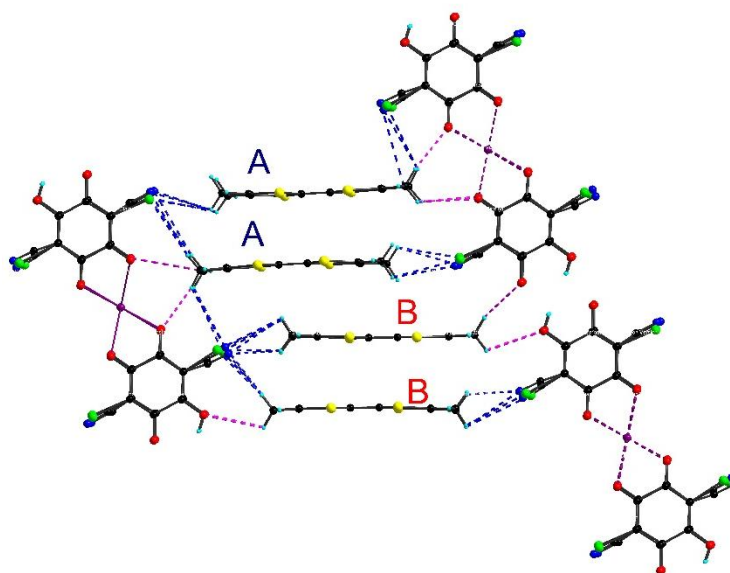
**Figure 2.** View of the crystal structure of compound **1** along *a* (left). Short S...S contacts (Å) between AA and BB dimer molecules shorter than sum of van der Waal radii (3.65): S1A-S4A 3.57; S2A-S3A 3.62; S5B-S8B 3.45; S6B-S7B 3.53 (right).

In the HCICNAn<sup>-</sup> anions, Cl and CN groups occupy the same atomic positions with occupancy factors of 0.5 as commonly found in CICNAn-based structures.<sup>34,38,39</sup> There are three types of C-O bond distances observed in the anilate ligand: C-O bond distances between 1.220(6)- 1.248(9) Å indicating the presence of C=O bonds, slightly longer C-O distances (1.302(1) Å and 1.312(8) Å) indicating C-OH bonds and two other C-O bond distances between 1.260(8)-1.288(11) Å with an intermediate value between C-OH and C-O<sup>-</sup> (Table S1). The K<sup>+</sup> ion is surrounded by four HCICNAn<sup>-</sup> anions and is coordinated through eight O atoms, forming a cubic geometry, unlike the nine-coordinated tri-capped trigonal prismatic coordination geometry formed through O, Cl and N atoms observed in the precursor KHClCNAn molecule (Figure 3).<sup>31</sup> Furthermore, in comparison with the crystal structure of the precursor, K<sup>+</sup>...Cl and K<sup>+</sup>...N-C contacts are absent, while K<sup>+</sup>...O distances range between 2.746(4) Å – 2.878(6) Å, giving rise to slightly distorted cubic geometry. Two HCICNAn<sup>-</sup> molecules on each side of the central K<sup>+</sup> cation are arranged in face-to-face manner forming  $\pi$ - $\pi$  interactions between the benzoquinoid rings and further engaged in strong intra/intermolecular hydrogen bonding interactions (O-H...O-C) (Figure 3).



**Figure 3.** Structure of  $\text{K}(\text{HCICNAn})_4$  anionic cluster, highlighting the slightly distorted cubic geometry of central  $\text{K}^+$  cation and intra/inter hydrogen bonding interactions ( $\text{\AA}$ ) in blue ( $\text{C}_{23}\text{-O}_4\cdots\text{H}_4\text{-O}_3$  2.19;  $\text{C}_{30}\text{-O}_7\cdots\text{H}_8\text{-O}_8$  2.18) and pink ( $\text{C}_{30}\text{-O}_7\cdots\text{H}_3\text{-O}_3$  2.02;  $\text{C}_{23}\text{-O}_4\cdots\text{H}_8\text{-O}_8$  2.03) respectively.

In addition, anion-donor interactions are present through hydrogen bonding between the methyl groups of TM-TTF donors and chloro or nitrogen atoms of the anilate substituents ( $\text{C-H}\cdots\text{Cl/CN}$ ) and  $\text{C=O/O}^-$  groups of anilates ( $\text{C-H}\cdots\text{O}$ ) (Figure 4, Table S2, ESI). Furthermore,  $\text{S}\cdots\text{Cl/CN}$  are also observed between S atoms of TM-TTF and Cl and CN substituents from the anilate ligand (Table S3, ESI).



**Figure 4.** Interactions between donor molecules and  $\text{K}(\text{HCICNAn})_4$  anions.  $\text{O}\cdots\text{H}$  and  $\text{Cl/N}\cdots\text{H}$  ( $d < 4 \text{\AA}$ ) are represented in pink and blue, respectively.

Compound **2** crystallizes in the monoclinic  $C2/c$  space group with half molecule of anionic ferrate complex and two and half independent molecules of TM-TTF organic donors A, B and C, respectively (Figure S3, ESI). The SQUEEZE program has been used and two molecules of DCM have been integrated, leading to the formula  $[\text{TM-TTF}]_5[\text{Fe}(\text{CICNAn})_3]\cdot(\text{CH}_2\text{Cl}_2)_2$ .

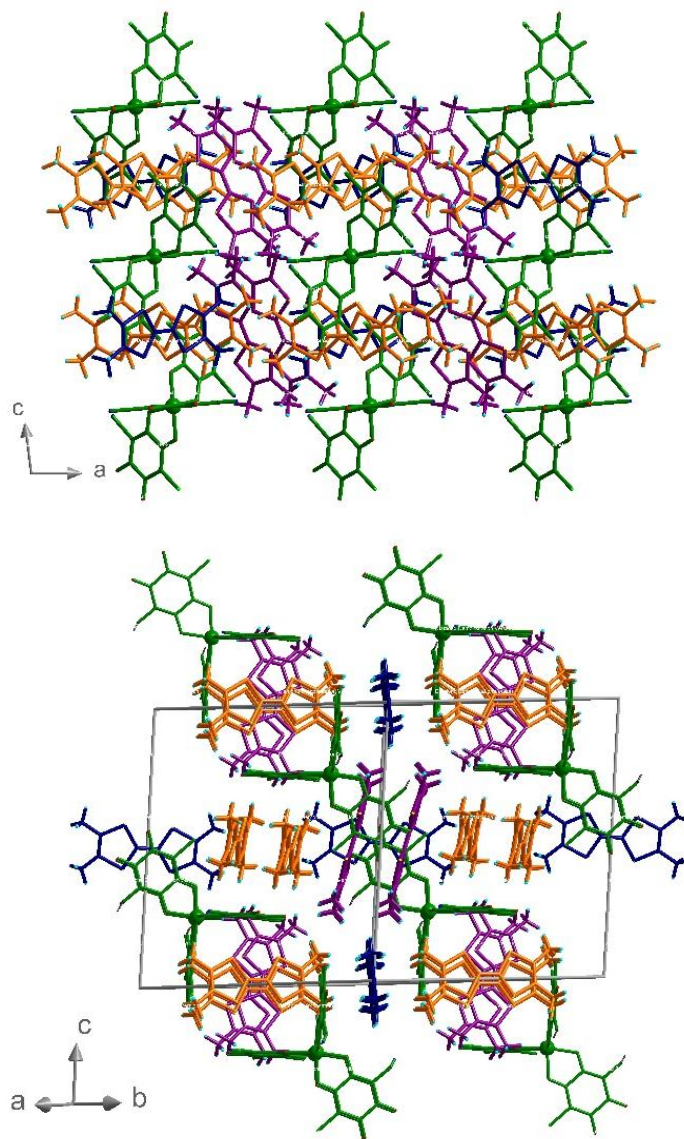
The inorganic layers consist of tris(chlorocyananilate)  $\text{Fe}^{\text{III}}$  complex, formed by three bidentate  $\text{CICNAn}^{2-}$  ligands chelated to  $\text{Fe}^{\text{III}}$  resulting in a octahedral geometry. Chloro and cyano substituents in the anilate ligands are distributed over two positions as in **1**. In the crystal structure, the anionic complexes are present as both  $\Lambda$  and  $\Delta$  enantiomers, with shortest intermolecular  $\text{Fe}\cdots\text{Fe}$  distances of *ca.* 12.819(1)  $\text{\AA}$  (Figure S4-S6).  $\text{Fe-O}$  bond distances are 2.025(5), 2.045(4) and 2.047(5)  $\text{\AA}$ . In the anilate ligand, terminal C-O bond distances are found in the 1.207(10)-1.231(12)  $\text{\AA}$  range, while two of the C-O bonds involving O atoms coordinated to  $\text{Fe}^{\text{III}}$



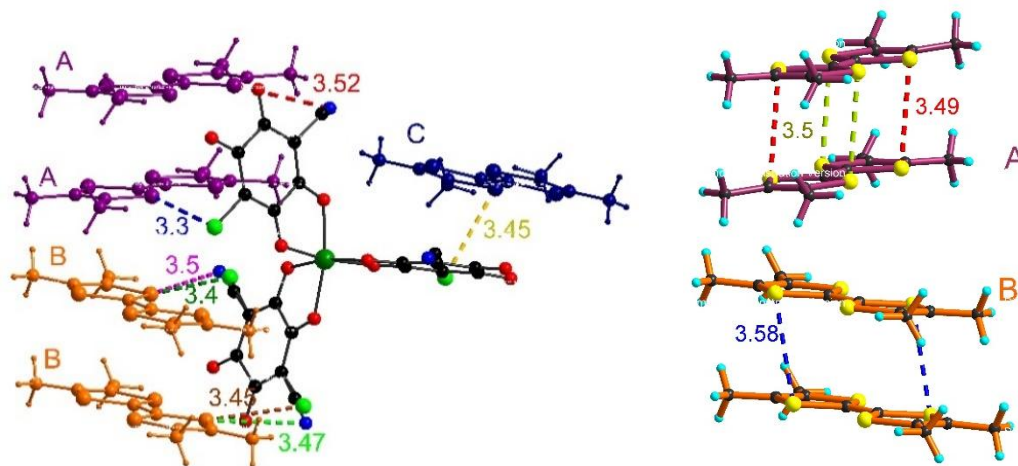
are slightly longer (1.264(7)-1.269(10) Å). However the third one is shorter (1.234(8) Å) because of the partial double bond character (Table S4).<sup>31,35</sup>

The formula indicates a total charge of +3 for five TM-TTF donor molecules. The C=C and C-S bond distances of TM-TTF (Table S5) suggest different oxidation states for donors A, B and C, with donor C bearing a more positive charge than A and B. However, a more precise charge assignment on each TM-TTF based on the  $Q = 6.347 - 7.4638 \cdot \delta$  formula<sup>49,50</sup> is difficult to attain because of the somehow large esd values on the C=C bonds.

The crystal packing is uncommon, with no segregation of organic donors and inorganic anionic complexes (Figure 5a). Columns of metal complexes run along *a* and *c* axes, surrounded by dimers of AA, BB and C donor molecules in the *ac* plane (Figure 5b, Figure S5).



**Figure 5.** Crystal packing of compound 2. Metal complexes and A-C donor molecules are coloured in green, purple, orange and blue respectively.

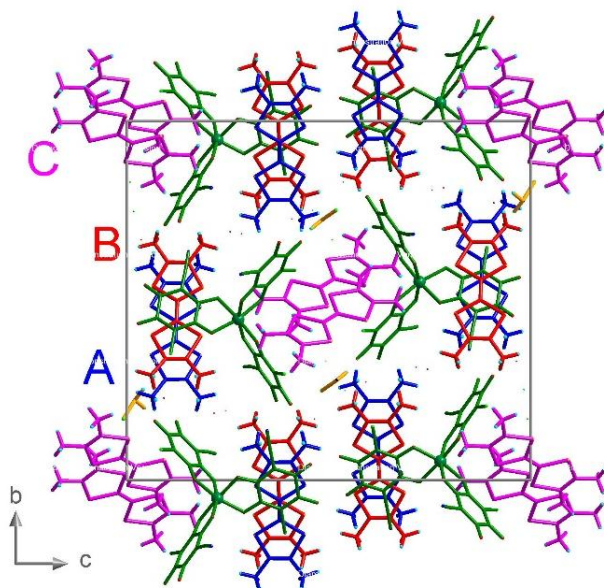


**Figure 6.** Intermolecular S...Cl/N interactions.  $S_{2A}-N_1$  3.52,  $S_{1A}-Cl_1$  3.30,  $S_{7B}-Cl_3$  3.4,  $S_{7B}-N_3$  3.5,  $S_{8B}-Cl_3$  3.47  $S_{8B}-N_3$  3.45 Å (left). Short S...S contacts in AA and BB dimers.  $S_{1A}-S_{4A}$  3.50,  $S_{2A}-S_{3A}$  3.49,  $S_{5B}-S_{8B}$  3.58 Å. Metal complexes and A-C donor molecules are coloured in green, purple, orange and blue respectively (right).

AA and BB dimers are arranged in edge to face manner with two  $CICNAn^{2-}$  ligands and C molecules are arranged in face to face manner with one  $CICNAn^{2-}$  ligand (Figure 6, Figure S5). This peculiar arrangement favors various intermolecular donor-anion interactions between S atoms from A, B and C donor molecules and the chloro/cyano substituents from the anilate ligands (S...Cl/N). Moreover, intermolecular hydrogen bonds are also observed between terminal methyl group of TM-TTF and chloro/cyano substituents (C-H...Cl/N) and C=O/O<sup>-</sup> groups of anilate. Dimers of AA and BB donors are arranged almost orthogonal to each other.

Compound **3** crystallizes in the monoclinic  $P2_1/n$  space group. The asymmetric unit consists of one  $[Fe(CICNAn)_3]^{3-}$  anionic complex and three TM-TSF donor molecules, indicated as A-C, along with crystallization solvent molecules (half molecules of dichloromethane and five water molecules with 0.5 occupancy), giving the formula  $[TM-TSF]_3[Fe(CICNAn)_3] \cdot (CH_2Cl_2)_{0.5}(H_2O)_{2.5}$  (Figure S7).

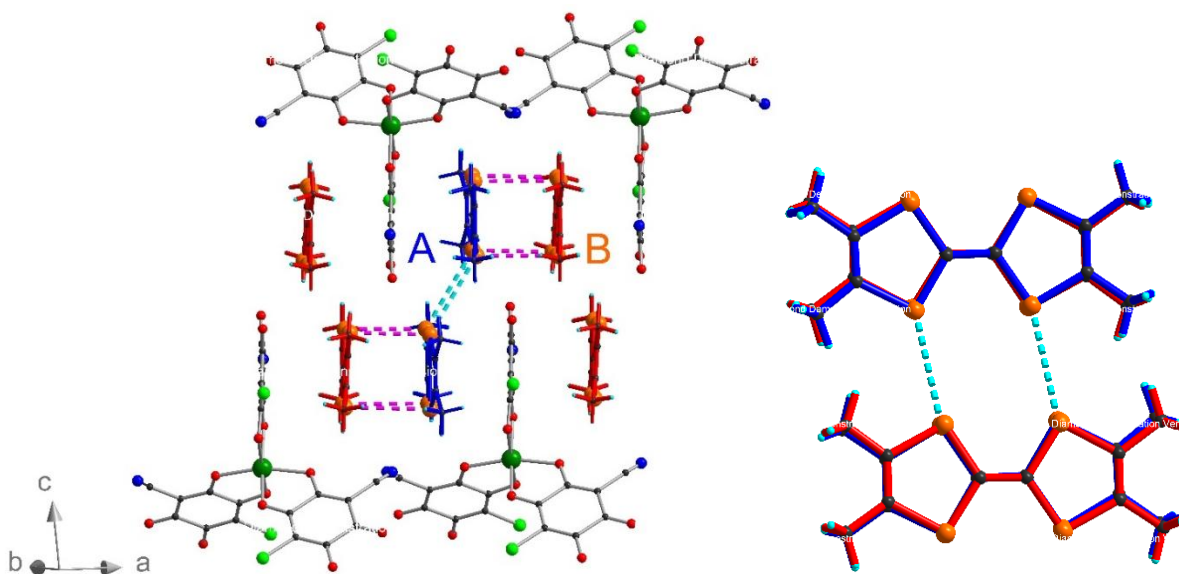
The crystal structure consists of TM-TSF donor molecules and  $[Fe(CICNAn)_3]^{3-}$  anionic complexes with no donor-anion segregation (Figure 7). Like in compound **2**, the inorganic layer is formed by octahedral  $[Fe(CICNAn)_3]^{3-}$  complexes with alternated  $\Lambda$  and  $\Delta$  enantiomers. The shortest intermolecular Fe...Fe distances is 11.530(4) Å and corresponds to the distance between metals of opposite chirality (Figure S8). Fe-O bond distances range between 1.991(10)-2.043(11) Å (Table S6). In the anilate ligand, C-O bond distances ranging between 1.192(20)-1.233(27) Å correspond to the terminal C=O bond, while C-O bonds in the vicinity of Fe<sup>III</sup> are slightly longer, 1.272(19)-1.292(16) Å (Table S6), as seen in previously reported metal complexes.<sup>34</sup>



**Figure 7.** View of the crystal structure of compound **3** along *a*. Metal complexes and A-C donors are indicated in green, blue, red and pink respectively.

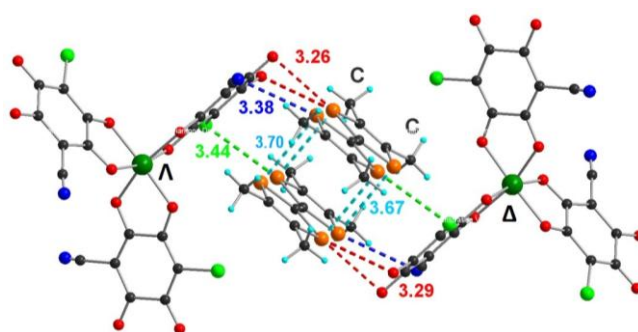
Taking into account the stoichiometry 3:1 of the salt, it can be deduced that each TM-TSF donor possesses a +1 charge, a more precise assignment by considering the C=C and C-Se bond distances (Table S7) being too inaccurate because of the lower quality of the structure.

In the crystal packing, slightly slipped metal complexes of  $\Lambda$  and  $\Delta$  enantiomers run along the *b* and *c* axes, with two opposite enantiomers separated by dimers of C molecules in the *bc* plane, while the other donors form B-A-A-B tetramers. Water and dichloromethane solvent molecules are arranged between donors and anion molecules (Figure 8).



**Figure 8.** Intramolecular Se...Se contacts ( $\text{\AA}$ ) less than van der Waals radii ( $4 \text{ \AA}$ ) in BAAB tetramers (left).  $\text{Se}_{2\text{A}}\text{-Se}_{4\text{A}}$  3.88,  $\text{Se}_{2\text{A}}\text{-Se}_{2\text{B}}$  3.36,  $\text{Se}_{4\text{A}}\text{-Se}_{4\text{B}}$  3.39,  $\text{Se}_{1\text{A}}\text{-Se}_{1\text{B}}$  3.57,  $\text{Se}_{3\text{A}}\text{-Se}_{3\text{B}}$  3.58  $\text{\AA}$ . Front view of BAAB tetramer showing good overlap between donors (right). A-B donors are indicated in blue and red respectively.

CC dimers are arranged in face-to-face manner showing strong Se...Se contacts ( $3.677(2)$  and  $3.702(2) \text{ \AA}$ ), shorter than the sum of van der Waals radii of two Se atoms ( $4 \text{ \AA}$ ). These dimers interact laterally with anions through several interactions such as Se...Cl ( $3.444(5) \text{ \AA}$ ), Se...N ( $3.382(19) \text{ \AA}$ ) and Se...O ( $3.290(15) \text{ \AA}$ ) (Figure 9). A similar arrangement is seen in  $[\text{BEDT-TTF}]_3[\text{Fe}(\text{Cl}_2\text{An})_3]\cdot 3\text{CH}_2\text{Cl}_2\cdot \text{H}_2\text{O}$ .<sup>34</sup>

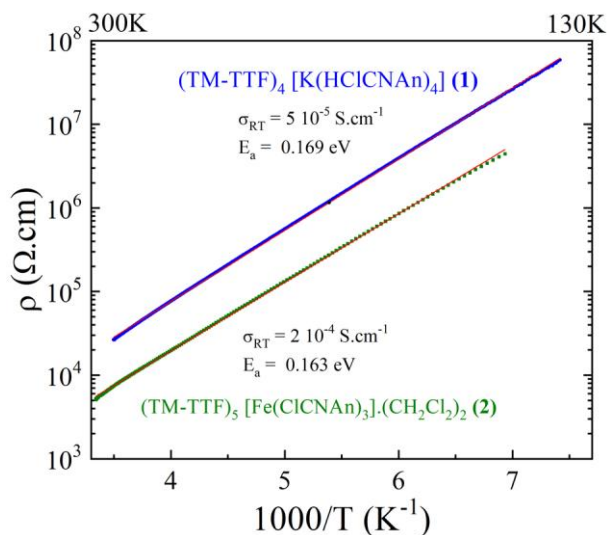


**Figure 9.** Intermolecular interactions between CC dimers surrounded by metal complexes of opposite chirality in compound **3** are highlighted. Se...Se, O...Se, Cl...Se, N...Se contacts are represented in cyan, red, green and blue, respectively.  $\text{Se}_{2\text{C}}\text{-Se}_{3\text{C}}$  3.67,  $\text{Se}_{1\text{C}}\text{-Se}_{4\text{C}}$  3.70,  $\text{Se}_{3\text{C}}\text{-O}_3$  3.29,  $\text{Se}_{3\text{C}}\text{-O}_4$  3.26,  $\text{Se}_{1\text{C}}\text{-N}_1$  3.38,  $\text{Se}_{2\text{C}}\text{-Cl}_1$  3.44.

In addition, several intermolecular hydrogen bond interactions are observed in the crystal packing between i) solvent and terminal methyl group of donor molecules ( $\text{Cl}\cdots\text{H-C}$ ;  $\text{O}\cdots\text{H-C}$ ); ii) solvent and  $\text{C}=\text{O}/\text{O}^-$  and chloro/cyano substituents from anion ( $\text{Cl}\cdots\text{H-C}$ ;  $\text{N}\cdots\text{H-C}$ ;  $\text{O}\cdots\text{H-C}$ ); iii) donor-anion interactions ( $\text{N}\cdots\text{H-C}$ ;  $\text{O}\cdots\text{H-C}$ ) ( $<3 \text{ \AA}$ ) (Figure S9-S10, Table S8, ESI).

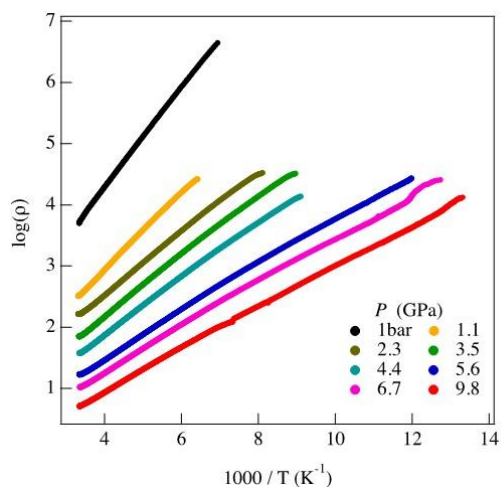
### 3.3 Single-Crystal Conductivity

The conducting properties of compounds **1** and **2** could be investigated thanks to single crystal resistivity measurements. Unfortunately, crystals of compound **3** were too small for such measurements. However, when considering the full oxidation state of TM-TSF donors and their dimerization, it can be safely inferred that compound **3** should be at most a very poor semiconductor. Ambient pressure temperature dependent resistivity measurements show that both compounds **1** and **2** are semiconductors with room temperatures conductivities of ca.  $5 \times 10^{-5} \text{ S cm}^{-1}$  for **1** and  $2 \times 10^{-4} \text{ S cm}^{-1}$  for **2** (Figure 10 and S11). Activation energies ( $E_a$ ) of ca. 1960 K (0.169 eV) and 1900 K (0.163 eV) have been calculated for **1** and **2**, respectively.



**Figure 10.** Temperature dependent single crystal electrical resistivity of compounds **1** and **2**. The red lines are the linear fit giving the activation energy  $E_a$  from the law  $\rho = \rho_0 \exp(E_a/T)$ .

A constant increase of the conductivity value under pressure is observed for compound **2**, yet it keeps its semiconducting character (Figure 11 and S12). At a pressure as high as 9.8 GPa, its room temperature conductivity value reaches  $0.2 \text{ S cm}^{-1}$ , and  $E_a$  is 795K.



**Figure 11.** Pressure and temperature dependent single crystal electrical resistivity of compound **2**.

When considering the lack of donors/anions segregation in the structure of **2**, the question whether the anion layer contributes to the conducting properties might arise.

#### 4. CONCLUSIONS

Three novel radical-cation salts based on TM-TTF and TM-TSF with chlorocyananilate ligand or/and tris(chlorocyananilato)ferrate(III) in THF/DCM solvent mixtures yielded purely organic and hybrid organic/inorganic molecular conductors, with unusual donor-anion stoichiometric ratios of 4:1, 5:1 and 3:1 for compounds **1-3**, respectively. Compound **1** shows segregation of TM-TTF donors and  $K(HClCNAn)_4$  anionic layers in the *bc* plane. The organic layers consist of mixed-valence TM-TTF donors arranged in  $\cdots AAB B \cdots$  repeating units and anionic layers formed by  $K(HClCNAn)_4$ , where four HClCNAn molecules are coordinated to a central  $K^+$  cation yielding a cubic coordination geometry, favouring several intermolecular donor-anion and hydrogen interactions. Compounds **2** and **3** consist of hybrid organic/inorganic layers with uncommon crystal packing, where no segregation of  $[Fe(ClCNAn)_3]^{3-}$  anionic complexes and TM-TTF/TM-TSF donors is observed. By changing S with Se atoms in the donors while keeping the same experimental conditions (anions and solvents), two different compounds have been obtained with different D:A stoichiometric ratios of 5:1 and 3:1 for TM-TTF and TM-TSF donors, respectively. Interestingly TM-TTF donors show mixed valence in compound **2**. Crystallization solvent molecules (dichloromethane, DCM and water) lead to various intermolecular interactions with donors and anions in compound **3**. Electron transport measurements on compounds **1** and **2** indicate semi-conducting behaviour, as it could have been expected from the crystal packing. These results pave the way to design a rich variety of new molecular conductors by combining TTF/TSF-based donors with anilate derivatives. We are currently working on the combination of TM-TSF and TM-TTF donors with other  $H_2X_2An$  ( $X = Cl, Br, I, \text{thiophene, etc.}$ ) anilate derivatives for a deep insight of the role of electron withdrawing/electron donating substituents on the structure/transport properties relationships. Furthermore, these donors could be combined with other anilate-based complexes  $[M(X_2An)_3]^{3-}$ ;  $M = Fe, Cr.. X = Cl, Br, I, \text{etc.}$ ) in order to design novel multifunctional materials where different physical properties can coexist or interplay.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Additional figures and tables as mentioned in the text (PDF).

### Accession Codes

CCDC 2012015 (**1**), 2012016 (**2**) and 2012017 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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## Notes

There are no conflicts to declare.

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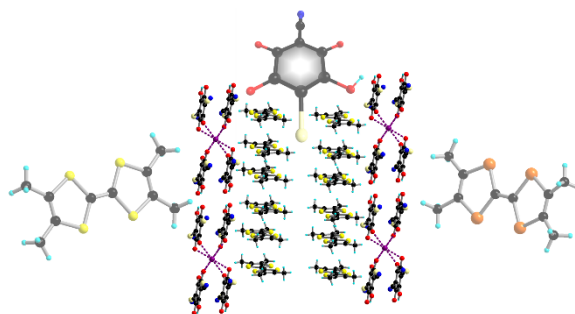
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### Radical Cation Salts of Tetramethyl-tetrathiafulvalene (TM-TTF) and Tetramethyl-tetraselenafulvalene (TM-TSF) with Chlorocyananilate-based Anions

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Crystalline molecular semiconductors with diverse donor:anion stoichiometry have been prepared by electrocrystallization of TM-TTF and TM-TSF with chlorocyananilate anion and its Fe<sup>III</sup> anion complex.