Radical Cation Salts of Tetramethyltetrathiafulvalene (TM-TTF) and Tetramethyltetraselenafulvalene (TM-TSF) with Chlorocyananilate-Based Anions

Suchithra Ashoka Sahadevan, Alexandre Abherve, Noemi Monni, Pascale Auban-Senzier, Hengbo Cui, Reizo Kato, Maria Laura Mercuri,* and Narcis Avarvari*

1. INTRODUCTION

Molecular conductors have attracted special interest in materials chemistry since the discovery of the first purely organic metallic conductor with the TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) charge transfer salt and superconductivity behavior in the [TM-TTF]_2[(H3O)Fe(C2O4)_3] charge transfer salt and superconductivity behavior in the [TM-TTF]_2[(H3O)Fe(C2O4)_3] charge transfer salt and superconductivity behavior in the [TM-TTF]_2[(H3O)Fe(C2O4)_3] charge transfer salt and superconductivity behavior in the [TM-TTF]_2[(H3O)Fe(C2O4)_3]. The functionalization of the TTF moiety gives the possibility to design multifunctional materials, where different physical properties coexist in the same crystal lattice. A plethora of anions, ranging from simple mononuclear complexes such as [MnCl6]_4^− (M = Mn, Fe, Co, Cr) and [MnCl6]_4^−, to bimetallic layered coordination polymers, have been used in combination with TTF derivatives to provide magnetic conductors, such as (BEDT-TTF)$_2$[(H$_2$O)Fe(C$_2$O$_4$)$_3$]·PhCN (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene, C$_2$O$_4$$^{2−}$ = oxalate), the first molecular paramagnetic superconductor, and (BEDT-TTF)$_2$[FeBr$_4$] (BETS = bis(ethylenedithio)tetrathiafulvalene), the first molecular antiferromagnetic superconductor, and (BEDT-TTF)$_2$[MnCr(C$_2$O$_4$)$_3$], the first molecular ferromagnetic metal. More often, it is generally observed that a donor:anion stoichiometric ratio of 2:1 and a partially oxidized/mixed-
valence oxidation state on donor molecules yield high electrical conductivity.\(^1\)\(^-\)\(^4\) However, radical cation salts with different donor:anion stoichiometric ratios, showing interesting conducting properties, have been reported, such as \((\text{TMTSF})\(_2\)\text{Cu(Adcmyp)}\(_4\)) \(\) with a 5:4 donor:anion ratio, giving an electrical conductivity \(\sigma_{\text{dc}}\) of 134 S cm\(^{-1}\).\(^1\)\(^0\)

Among the anions used so far,\(^7\)\(^-\)\(^28\) 3,6-disubstituted 2,5-dihydroxy-1,4-benzoquinones, also known as anilates,\(^29\) have attracted interest in the molecular conductors field thanks to their redox behavior and their versatility in changing the substituents (halogens, cyano, thiophene, etc.)\(^30\)\(^-\)\(^31\) at the 3,6-positions of the anilato moiety, which can give rise to different intermolecular interactions.\(^32\)\(^-\)\(^36\) Additionally, anilate derivatives are interesting building blocks for the design of various multifunctional materials showing luminescence,\(^37\)\(^-\)\(^45\) magnetism, or/and conductivity.\(^41\)\(^-\)\(^45\) Pioneering 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.\(^46\)

Recently, some of us have reported on purely organic and hybrid organic/inorganic compounds based on anilate derivatives with BEDT-TTF.\(^33\)\(^-\)\(^34\)\(^-\)\(^36\) Accordingly, radical cation salts of BEDT-TTF with chlorocyananilate (KHClCNAn\(^\)\) and chloranilate (HCl\(_2\)An\(^\)\) were obtained by combining BEDT-TTF with \([\text{Fe}(\text{X}2\text{An})]_3\) (X = Cl, Cl/CN), giving rise to different donor:anion stoichiometric ratios such as 3:1, 6:1, 4:1, 5:2, etc.\(^33\)\(^-\)\(^34\)

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 \([\text{TM-TTF}]_5[\text{Fe(CICNAn)}]_3\) \(\) (1), \([\text{TM-TTF}]_5[\text{Fe(CICNAn)}]_3\cdot2\text{CH}_2\text{Cl}_2\) \(\) (2), and \([\text{TM-TSF}]_5[\text{Fe(CICNAn)}]_3\cdot0.5\text{CH}_2\text{Cl}_2\cdot2\text{H}_2\text{O}\) \(\) (3). The last compound represents the first example of a radical cation salt based on TM-TSF and anilate derivatives. A thorough structural characterization of compounds 1–3, with a special emphasis on the intermolecular interactions, and a study of their transport properties are discussed herein.

### 2. EXPERIMENTAL SECTION

#### 2.1. Materials and Methods.\(^\) KHClCNAn and \((\text{PPh}_4)_3[\text{Fe(CICNAn)}]\) were prepared according to the procedure described in the literature.\(^31\) TM-TTF and TM-TSF were obtained commercially. Crystals were obtained by using the electrocrystallization technique.

#### 2.2. Synthetic Procedures.\(^\) \([\text{TM-TTF}]_5[\text{KHClCNAn}]_3\) \(\) (1), TM-TTF (0.0115 mmol) and KHClCNAn (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 1 week by applying 1 mA of current at 20 °C.

\[\text{[TM-TTF]}_5\text{[Fe(CICNAn)]}_3\cdot2\text{CH}_2\text{Cl}_2\] \(\) (2). Crystals of compound 2 were grown using conditions similar to those for 1, except that a \((\text{PPh}_4)_3[\text{Fe(CICNAn)}]\) solution (0.0115 mmol) was placed in the cathodic chamber instead of KHClCNAn.

\[\text{[TM-TSF]}_3\text{[Fe(CICNAn)]}_3\cdot0.5\text{CH}_2\text{Cl}_2\cdot2\text{H}_2\text{O}\] \(\) (3). Crystals of compound 3 were grown using conditions similar to those for 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 an Agilent Supernova diffractometer with Cu Kα radiation (\(\lambda = 1.54184\) Å) 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 Å\(^3\) 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 is given in Table 1.

#### 2.4. Single-Crystal Conductivity Measurements.\(^\) Resistivity measurements were undertaken on pure 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 homemade cryostat equipped with a 4 K probe tube using a Cernox sensor in good thermal contact with the samples as a 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 by attaching four 10 μm gold wires and gold paint on a single crystal with a size of 0.13 X 0.03 X 0.02 mm\(^3\). The sample was encapsulated with a mixture of epoxy and alumina. A diamond anvil with a cuvet size of 0.7 mm and tension-annealed SUS301 stainless steel 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 the tris(chlorocyananilato)ferrate(III) complex \((\text{PPh}_4)_3[\text{Fe(CICNAn)}]\) in a THF/DCM mixture yielded the radical cation salts \([\text{TM-TTF}]_5[\text{KHClCNAn}]_3\) \(\) (1), \([\text{TM-TTF}]_5[\text{Fe(CICNAn)}]_3\cdot2\text{CH}_2\text{Cl}_2\) \(\) (2), and \([\text{TM-TSF}]_5[\text{Fe(CICNAn)}]_3\cdot0.5\text{CH}_2\text{Cl}_2\cdot2\text{H}_2\text{O}\) \(\) (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 2).
Attempts to electrocrystallize TM-TSF with KHClCNAn were unsuccessful so far.

3.2. Solid-State Structures. Single-crystal X-ray studies show that compound 1 crystallizes in the triclinic space group $P\overline{1}$, with two independent TM-TTF donor molecules (A and B), two HClCNAn$^{-}$ anions, and a half potassium cation $K^+$ in the asymmetric unit, leading to the formula $[\text{TM-TTF}]_4[\text{K(HClCNAn)}]_4$ (Figure 1).

In the crystal packing, there is segregation between TM-TTF donor molecules and K(HClCNAn)$_4$ anionic clusters in the $bc$ plane, where columns of donors alternate with columns of anions (Figure 2a). The central C=\text{C} and internal C=S bond lengths of the TM-TTF molecules indicate a mixed valence oxidation state for the 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.

Table 1. Crystallographic Data of Compounds 1–3

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<td>$S(F2)$, all data</td>
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$R1(F) = \sum||F_o|| - ||F_c||/\sum||F_o||$.

$wR2(F) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

$S(F2) = [\sum w(F_o^2 - F_c^2)^2/(n + r - p)]^{1/2}$.

Table 2. Precursors and Synthetic Conditions Used for Compounds 1–3

<table>
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<tr>
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<th>donor (D)</th>
<th>TM-TTF</th>
<th>TM-TSF</th>
<th>D:A ratio</th>
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<td>KHClCNAn</td>
<td>[TM-TTF]$_4$[K(HClCNAn)$_4$] (1)</td>
<td>1:3</td>
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<tr>
<td>[Fe(ClCNAn)$_3$]$^{-}$</td>
<td>[TM-TTF]$_4$[Fe(ClCNAn)$_3$]·2CH$_2$Cl$_2$ (2)</td>
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<td>[TM-TSF]$_4$[Fe(ClCNAn)$_3$]·0.5CH$_2$Cl$_2$·2.5H$_2$O (3)</td>
<td>1:1</td>
<td></td>
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</table>

*Experimental conditions: solvent, THF/DCM; current, 1 μA.*
The organic donor layers are formed by alternating slipped dimers AA and BB in the bc plane, with short intermolecular S···S contacts (less than the sum of van der Waal radii of 3.65 Å), favoring β′ packing (Figure 2b and Figures S1 and S2 in the Supporting Information). Along the stack, the donor molecules are arranged in …AABB… repeating units.

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

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 (C–H···Cl/CN) and C=O/O⁻ groups of anilates (C–H–O).
atoms of TM-TTF and Cl and CN substituents from the anilate ligand (Table S3 in the Supporting Information).

Compound 2 crystallizes in the monoclinic space group C2/c with a half-molecule of the anionic ferrate complex and two and a half independent molecules of TM-TTF organic donors A−C, respectively (Figure S3 in the Supporting Information). The SQUEEZE program has been used and two molecules of DCM have been integrated, leading to the formula [TM-TTF]5[Fe(ClCNAn)3]·2CH2Cl2.

The inorganic layers consist of a tris(chlorocyananilate) FeIII complex, formed by three bidentate ClCNAn 2− ligands chelated to FeIII, resulting in an 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 Λ and Δ enantiomers, with the shortest intermolecular Fe−Fe distances of ca. 12.819(1) Å (Figures S4−S6). Fe−O bond distances are 2.025(5), 2.045(4), and 2.047(5) Å. In the anilate ligand, terminal C−O bond distances are found in the 1.207(10)−1.231(12) Å range, while two of the C−O bonds involving O atoms coordinated to FeIII are slightly longer (1.264(7)−1.269(10) Å). However, the third bond is shorter (1.234(8) Å) because of the partial double-bond character (Table S4).

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−C, with donor C bearing a more positive charge in comparison to A and B. However, a more precise charge assignment on each TM-TTF based on the Q = 6.347 − 7.46386 formula is difficult to attain because of the somewhat 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 the a and c axes, surrounded by dimers of AA, BB, and C donor molecules in the ac plane (Figure 5b and Figure S5).

AA and BB dimers are arranged in an edge-to-face manner with two ClCNAn2− ligands, and C molecules are arranged in a face-to-face manner with one ClCNAn2− ligand (Figure 6 and Figure S5). This peculiar arrangement favors various intermolecular donor−anion interactions between S atoms from donor molecules A−C and the chloro/cyano substituents from the anilate ligands (S···Cl/N). Moreover, intermolecular hydrogen bonds are also observed between the terminal methyl group of TM-TTF and chloro/cyano substituents (C−H···Cl/N) and C=O/O− groups of anilate. Dimers of AA and BB donors are arranged almost orthogonal to each other.

Compound 3 crystallizes in the monoclinic space group P21/n. The asymmetric unit consists of one [Fe(ClCNAn)3]3− anionic complex and three TM-TSF donor molecules, indicated as A−C along with crystallization solvent molecules (a half molecule of dichloromethane and five water molecules with 0.5 occupancy), giving the formula [TM-TSF][Fe(ClCNAn)3]·0.5CH2Cl2·2.5H2O (Figure S7).

The crystal structure consists of TM-TSF donor molecules and [Fe(ClCNAn)3]3− anionic complexes with no donor−anion segregation (Figure 7). As in compound 2, the inorganic layer is formed by octahedral [Fe(ClCNAn)3]3− complexes with alternating Λ and Δ enantiomers. The shortest intermolecular Fe···Fe distance is 11.530(4) Å and corre-
sponds to the distance between metals of opposite chirality (Figure S8). Fe−O bond distances range between 1.991(10) and 2.043(11) Å (Table S6). In the anilate ligand, C−O bond distances ranging between 1.192(20) and 1.233(27) Å correspond to the terminal C=O bond, while C−O bonds in the vicinity of FeIII are slightly longer, 1.272(19)−1.292(16) Å (Table S6), as seen in previously reported metal complexes.34

When the 3:1 stoichiometry of the salt is taken into account, it can be deduced that each TM-TSF donor possesses a +1 charge, a more precise assignment by consideration of 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 Λ and Δ 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).

CC dimers are arranged in a face-to-face manner showing strong Se···Se contacts (3.677(2) and 3.702(2) Å), shorter than the sum of van der Waals radii of two Se atoms (4 Å). These dimers interact laterally with anions through several interactions such as Se···Cl (3.444(5) Å), Se···N (3.382(19) Å), and Se···O (3.290(15) Å) (Figure 9). A similar arrangement is seen in [BEDT-TTF]3[Fe(Cl2An)3]·3CH2Cl2·H2O.34

In addition, several intermolecular hydrogen bond interactions are observed in the crystal packing between (i) the solvent and terminal methyl groups of donor molecules (Cl···H−C; O···H−C), (ii) the solvent and C=O/O− and chloro/cyano substituents from the anion (Cl···H−C; N···H−C; O···H−C), and (iii) donor−anion interactions (N···H−C; O···H−C) (<3 Å) (Figures S9 and S10 and Table S8 in the Supporting Information).

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 the full oxidation state of TM-TSF donors and their dimerization are considered, 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 temperature conductivities of ca. 5×10−5 Sc m−1 for 1 and 2×10−4 Sc m−1 for 2 (Figure 10 and Figure S11). Activation energies (Ea) of ca. 1960 K (0.169 eV) and 1900 K (0.163 eV) have been calculated for 1 and 2, respectively.

A constant increase in the conductivity value under pressure is observed for compound 2, yet it keeps its semiconducting character (Figure 11 and Figure S12). At a pressure as high as 9.8 GPa, its room-temperature conductivity value reaches 0.2 S cm−1, and the Ea value is 795 K.

When the lack of donor/anion segregation in the structure of 2 is considered, a question of 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 a 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 the 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 ···AABB··· 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, favoring 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(CICNAn)₃]³⁻ anionic complexes and TM-TTF/TM-TSF donors is observed. By a change of the S with Se atoms in the donors while the same experimental conditions are kept (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. Solvent molecules of crystallization (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 semiconducting behavior, as 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 H₂X₂An (X = Cl, Br, I, thiophene, etc.) anilate derivatives for a deep insight into the role of electron-withdrawing/electron-donating substituents on the structure/transport property relationships. Furthermore, these
donors could be combined with other anilate-based complexes \([M(X_2An)_3]^-\) (\(M = \text{Fe, Cr, } \ldots; X = \text{Cl, Br, I, etc.}\)) 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 at https://pubs.acs.org/doi/10.1021/acs.cgd.0c00873.

Additional figures and tables as described in the text (PDF)

**Accession Codes**

CCDC 2012015−2012017 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, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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