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Synthesis Crystal Structures and Magnetic Properties of 2,3,6,7-Tetrakis(2-cyanoethylthio)tetrathiafulvalene Polymers

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Abstract. The detailed synthesis, crystal structures and magnetic properties of several transition metal complexes involving oxidized or neutral 2,3,6,7-Tetrakis(2-cyanoethylthio) tetrathiafulvalene (TCE-TTF) are presented. All compounds revealed polymeric arrangements with metal ions bridging TCE-TTF with Metal-Nitrogen bounds. Strong van-der-Waals interactions between polymers increased the dimensionality of the materials. The magnetic behaviour of hetero-bimetallic compound $[M(1)^{II}(TCE-TTF^{\bullet+})_2M(2)^{II}(H_2O)_4](ClO_4)_6 \cdot 2H_2O$ with $M=Zn/Mn$ is also studied.

INTRODUCTION

The TTF molecule (tetrathiafulvalene) and its derivatives are certainly one of the most popular units to build conducting molecular materials [1]. Vigorous research activity has been developed to synthesize materials in which several properties coexist, such as magnetism and electrical conductivity [2]. Magnetism in these kinds of materials is usually due to paramagnetic metals whereas conductivity is due to both the oxidation of TTF and the organization of $TTF^{\bullet+}$ radicals as networks [3]. One of the goals of these researches is to build the TTF derivatives network thanks to two different strategies: i) TTF derivatives and paramagnetic ions are separately packed; all interactions between mobile and localized electrons take place through space. ii) TTF derivatives and paramagnetic ions are chemically linked [4] To do so, numerous TTF derivatives bearing coordinating groups were synthesized.

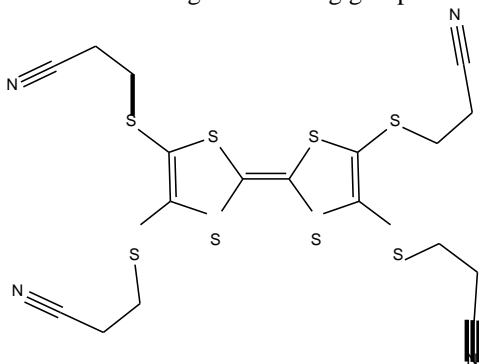


FIGURE 1. TCE-TTF molecule

This paper focuses on polymers based on TTF tetrathiolate 2,3,6,7-tetrakis(2-cyanoethylthio)tetrathiafulvalene (Scheme 1) abbreviated TCE-TTF, a TTF bearing four nitrilo groups able to coordinate a transition metal cation. This molecule is used as starting compound for numerous extended TTF synthesis, such as extended molecules, [5],[6] macrocyclic compounds, [7] layered TTF,[8] podand-TTFs [9]. To the best of our knowledge, this TTF derivative

was only reported as a component of cation radical salts [10],[11] as well as for tetrameric $[\text{Ag}(\text{TCE-TTF})_2]\text{SbF}_6$ [12], homo-metallic 3-D frameworks $\text{Ag}_4(\text{TCE-TTF}^0)_2(\text{CF}_3\text{SO}_3)_2(\text{CF}_3\text{SO}_3)_2$ [13] and pseudo 3-D compounds $[\text{M}^{\text{II}}(\text{TCE-TTF}^{\bullet+})_2\text{M}^{\text{II}}(\text{H}_2\text{O})_4](\text{X})_6 \cdot 2\text{H}_2\text{O}$, $\text{X}=\text{BF}_4^-$ for $\text{M}=\text{Co}^{\text{II}}$ or $\text{X}=\text{ClO}_4^-$ for $\text{M}=\text{Mn}^{\text{II}}$, Zn^{II} , or Cd^{II} [14]. In this work, heterometallic compounds isostructural to this pseudo 3-D series were studied with $\text{M} = \text{Mn}/\text{Co}$, Mn/Zn , Mn/Cd . Crystal structures of polymer with $\text{M} = \text{Co}_{3/8}, \text{Mn}_{5/8}$ (**1**), $\text{M} = \text{Zn}, \text{Mn}$ with $\text{Zn}/\text{Mn} < 1$ (**2**) and $\text{Zn}/\text{Mn} > 1$ (**3**), as well as the magnetic behaviour of (**2**) and (**3**) are presented. Synthesis and structures of a new diamagnetic pseudo 2D polymer $[(\text{TCE-TTF}^0)\text{Ag}_3(\text{CF}_3\text{SO}_3)_3] \cdot \text{CH}_3\text{OH}$ (**4**) and a 1D polymer $[(\text{TCE-TTF}^{\bullet+})\text{Zn}(\text{H}_2\text{O})_{2.9}(\text{HCIC-CHCl})_{1.1}](\text{ReO}_4)_3$ (**5**) are also presented. In compound (**5**), a chlorine containing ligand is obtained from the reduction of solvents with zinc.

EXPERIMENTAL

Synthesis of TCE-TTF-based polymers

The TTF molecule, functionalized with four electron-withdrawing 2-cyanoethylthio groups, 2,3,6,7-tetrakis(2-cyanoethylthio)tetrathiafulvalene (TCE-TTF) was prepared by the well-known triethylphosphite-based coupling reaction from a 3,4-cyanoethylthio-1,3-dithiole-2-one molecule inspired by J. Becher [15]. This type of arm has been successfully employed to coordinate transition metals and produced polymeric architectures. In the following, we will present the synthesis, crystal structure and magnetic characterizations of a series of isostructural hetero-bimetallic materials and diamagnetic metal-based silver and zinc polymer involving the radical form of TCE-TTF. Compounds **1-3** and **5** were obtained from neutral TCE-TTF and $\text{M}^{\text{II}}(\text{hfac})_2 \cdot x\text{H}_2\text{O}$, in chloride solvents with the electrocrystallization technique, and the co-crystallisation technique for the silver-containing compound **4**.

X-Ray data collection and structure determinations

Single crystals were mounted on a four circle diffractometer equipped with a CCD camera and a graphite monochromated $\text{MoK}\alpha$ radiation source ($\lambda = 0.71073 \text{ \AA}$). **1**, **2**, **4** and **5** were mounted on a Nonius Kappa CCD, and crystal of **3** was mounted on a Bruker-AXS APEXII, from the Centre de Diffractométrie (CDIFX), ISCR, Université de Rennes 1, France. Crystals of **2** and **3** were mounted on a cryoloop and cooled at 100K in a liquid nitrogen stream, data of crystals **1**, **4** and **5** were collected at room temperature. The crystal structures were solved by direct method using SIR-97 program [16] and refined with full matrix least squares method on F^2 using SHELXL-97 program.[17]

Compounds **1**, **2** and **3** are isostructural. In compound **1**, three oxygen atoms O9, O10 and O11 of one ClO_4^- anion were splitted as two fragments A and B with calculated occupation factor of 0.79 and 0.21 respectively. For compound **1**, each metal site M(1) and M(2) is statistically occupied with two metals Co and Mn. The occupation factor of cobalt was refined and this of manganese was tied as the sum of occupation factor is restrained to unity. The same treatments were done for **2** and **3**, in which these positions are fulfilled with Zn and Mn. For compound **5**, Cl1/O16, and Cl2/O15 were restrained to fit the same position, the central Re2 of one ReO_4^- anion is splitted as two close ions Re2A and Re2B with respective occupation factors 0.82 and 0.18. All compounds crystallize with TCE-TTF molecules in which all the cyanoethylthio arms lies on the same side of the TTF mean plane.

RESULTS AND DISCUSSION

Series of compounds $[\text{M}(1)^{\text{II}}(\text{TCE-TTF}^{\bullet+})_2\text{M}(2)^{\text{II}}(\text{H}_2\text{O})_4](\text{ClO}_4)_6 \cdot 2\text{H}_2\text{O}$

Synthesis and structure

Years ago, we synthesized a series of TCE-TTF dia- and paramagnetic homo-metallic polymers $[\text{M}(1)^{\text{II}}(\text{TCE-TTF}^{\bullet+})_2\text{M}(2)^{\text{II}}(\text{H}_2\text{O})_4](\text{X})_6 \cdot 2\text{H}_2\text{O}$, with $\text{M}(1)=\text{M}(2)=\text{Co}^{\text{II}}$ for $\text{X}=\text{BF}_4^-$ and $\text{M}(1)=\text{M}(2)=\text{Mn}^{\text{II}}$, Zn^{II} or Cd^{II} for $\text{X}=\text{ClO}_4^-$. In these polymers, the asymmetric unit contains two metals ions located at two inversion centre sites, and the TCE-TTF is oxidized as a radical [11]. The octahedral coordination sphere of M(1) is built up with six nitrogen atoms from four TCE-TTF $^{\bullet+}$ radicals, the second metal ion M(2) is lying in a centrosymmetric coordination sphere built with four oxygen atoms from water molecules and, in apical position, two nitrogen atoms, belonging to two TCE-TTF $^{\bullet+}$ (see Figure 1). Due to different coordination spheres around M(1) and M(2), we envisaged to synthesize new isostructural

hetero-bimetallic (Mn/Co, Mn/Zn and Mn/Cd) compounds in which one type of metal ion fit one crystallographic site, the other metallic ion lying at the second crystallographic site.

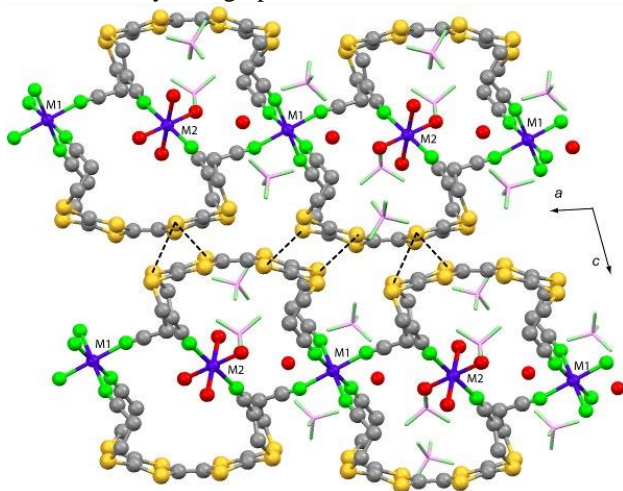


FIGURE 2. The two infinite 2-D polymeric networks range in the ab plane. Strong S...S interactions between them along c axis give a third dimension to the compound.

These polymers were obtained by electrocrystallisation technique: 10 mL of a solvent mixture (benzene/tetrachloromethane/dichloromethane 1/1/1) was added in each side of a U-shaped cell with two compartments separated by a glass frit. With much care, 80 mg of $[(C_4H_9)_4N]ClO_4$ was dissolved in each compartment, followed on the anode side by TCE-TTF (5 mg, 9.10^{-3} mmol). The two metallic ions were introduced as hexafluoroacetylacetonate (hfac) salts, depending on the expected ratio, with a total amount of $M^{II}(hfac)_2 \cdot xH_2O$ of 30mg with the starting ratio given in Table 1. Black crystals appeared shortly at the platinum anode after a $0.5 \mu A$ constant current was applied. Suitable crystals for X-Ray diffraction were obtained for three compounds within two weeks. The mean values obtained by Energy Dispersive Spectrometry technique (EDS) performed on three crystalline compounds metal ratio in the polymers are given in Table 1.

TABLE 1. Metal ratio in atomic % scale for $[M(1)^{II}(TCE-TTF^{\bullet+})_2M(2)^{II}(H_2O)_4](ClO_4)_6 \cdot 2H_2O$

| Metal | Starting materials ratio (atomic %) | EDS analysis atomic ratio (%) | M(1) site occupation (%) | M(2) site occupation (%) |
|-----------|-------------------------------------|-------------------------------|--------------------------|--------------------------|
| Mn/Co (1) | 50/50 | variable | 67/33 | 58/42 |
| Mn/Zn (2) | 50/50 | 78/22 | 92/8 | 70/30 |
| Mn/Zn | 17/83 | 46/54 | - | - |
| Mn/Zn | 7/93 | 31/69 | - | - |
| Mn/Zn (3) | 2/98 | 15/85 | 18/82 | 12/88 |
| Mn/Cd | 93/7 | 4/96 | - | - |

All compounds are isostructural to the homometallic materials previously reported, crystallographic data are given in Table 2. An ORTEP plot of the asymmetric unit of compound **1** with the atomic numbering scheme is shown in Figure 2. M(1) crystallographic site is surrounded by N2, N3 and N4 atoms in a centrosymmetric octahedral coordination sphere, six nitrogen atoms belong to four TCE-TTF radicals. M(2) is surrounded by two N1 atoms and four oxygen atoms from water molecules in a centrosymmetric octahedral coordination sphere.

TABLE 2. Crystal data and structure refinement parameters for compounds **1**, **2**, and **3**.

| Compound | 1 | 2 | 3 |
|---|--|--|--|
| Formula | C ₃₆ H ₄₄ Cl ₆ Co _{0.75} Mn _{1.25} N ₈ O ₃₀ S ₁₆ | C ₃₆ H ₄₄ Cl ₆ Zn _{0.38} Mn _{1.63} N ₈ O ₃₀ S ₁₆ | C ₃₆ H ₄₄ Cl ₆ Zn _{1.70} Mn _{0.30} N ₈ O ₃₀ S ₁₆ |
| Formula weight | 1907.32 | 1908.24 | 1922.06 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | P2 ₁ /c | P2 ₁ /c | P2 ₁ /c |
| a/Å | 13.1212(3) | 13.0984(18) | 13.124(5) |
| b/Å | 10.5214(2) | 10.3215(12) | 10.314(3) |
| c/Å | 26.8481(7) | 26.751(4) | 26.507(9) |
| β/° | 103.098(1) | 102.452(7) | 102.715(11) |
| V/Å ³ | 3610.04(14) | 3531.5(8) | 3500.1(19) |
| Z | 2 | 2 | 2 |
| Dc/g.cm ⁻³ | 1.755 | 1.795 | 1.824 |
| F(000) | 1931 | 1932 | 1945 |
| μ(Mo-Kα)/mm ⁻¹ | 1.160 | 1.204 | 1.430 |
| Total reflections | 16052 | 16853 | 25205 |
| Unique reflections | 8582 | 9306 | 7972 |
| I>2σ(I) | 4854 | 5377 | 5468 |
| No. of parameters | 475 | 447 | 447 |
| GOF on F ² | 1.092 | 1.052 | 1.070 |
| R1 ^a | 0.0586 | 0.0588 | 0.0619 |
| ωR ₂ ^b | 0.1627 | 0.1420 | 0.1529 |
| Δρ _{max} /Δρ _{min} /e.Å ⁻³ | 0.935 / -0.851 | 1.018 / -0.886 | 1.688 / -0.702 |

a R = Σ||Fo| - |Fc|| / Σ|Fo|. *b* wR₂ = {Σ[ω (Fo² - Fc²)²] / Σ[ω (Fo²)²]}^{1/2}

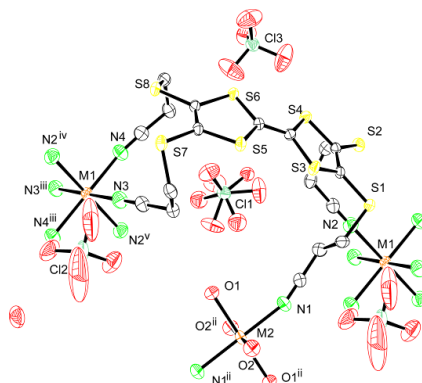


FIGURE 3. ORTEP (30% probability ellipsoids) structure of asymmetric unit of **1** at 293K, with labelling scheme and completed metal coordination spheres. Hydrogen atoms and non coordinated water molecules are omitted for clarity. Symmetry used: ii: 1-x, 2-y, 1-z; iii: 2-x, 1-y, 1-z; iv: 1+x, y, z; v: 1-x, 1-y, 1-z.

From the atomic ratio obtained from EDS (Table 1), one can notice that it does not fit the experimental starting ratio. For Mn-Co containing crystals, the ratio observed by the EDS techniques gives no homogenous values from one sample to another, this suggests that Mn^{II} and Co^{II} are interchangeable in the different [M(1)N₆] or [M(2)O₄N₂] octahedral coordination spheres, despite the slightly larger radius of the Mn^{II} ion: from X-rays in previous published homometallic compounds the M(2)-O and M(1)-N mean values (2.19 and 2.23 Å respectively at 100K for M=Mn) were found quite larger than those observed in Co-containing compounds (2.09 and 2.12 Å at the same temperature). For Mn-Cd containing series, a large excess of Mn^{II} in the electrolyte mixture Mn(hfac)₂.xH₂O/Cd(hfac)₂.xH₂O, reached to crystals mainly containing a large excess of Cd^{II}. Due to the low quality of these crystals, it was not possible to collect enough good data, however EDS showed the large amount of Cd in our samples. For Mn-Zn containing series, the Mn/Zn ratio in the crystals is increased compared to this used as starting reagents, the paramagnetic Mn^{II}

ion takes over diamagnetic Zn^{II} in the polymer. Only synthesis with negligible amount of Mn^{II} compared to Zn^{II} yield to crystals in which quantitative amount of Zn^{II} is observed. In homometallic compounds the radii of Mn^{II} is slightly larger (4%) than those of Zn^{II}, and those of Cd^{II} is larger than those of Mn^{II}. It seems that the size of the metal transition ion is the driving force for the auto-assembling of the polymer. Indeed, the polymers grow for larger ions. Radii of Co^{II}, Mn^{II}, Cd^{II} and Zn^{II} in octahedral coordination sphere taken from reference [18] are in line with those given in this text.

In the homometallic polymers, the X-ray analysis revealed that the [M(1)N₆] coordination sphere is larger than the [M(2)O₄N₂]. On Table 1, one can notice that the larger ion statistically prefers M(1) site whereas the M(2) crystallographic site. From crystallographic measurements, the occupation factor of M(1)/M(2) sites by the larger ion, is 0.67/0.38; 0.92/0.70; 0.18/0.12 for **1**, **2** and **3** respectively.

Magnetic measurements

The magnetization of compounds **2** and **3** have been measured on powders in the temperature range 2-300 K with an external dc field equal to 0.2 T below 20 K and equal to 1 T above 20 K. The temperature dependences of χ_M^{-1} for both compounds are plotted on Figure 3. The straight lines passing through the origin reflects Curie behaviour for both compounds in agreement with reported magnetic measurements on [Mn^{II}(TCE-TTF^{•+})₂Mn^{II}(H₂O)₄](ClO₄)₆•2H₂O. In this compound the Curie constant, C, is equal to 8.6 cm³ K mol⁻¹ which corresponds to the contribution of two isolated Mn^{II} spins. Magnetic measurements on [Zn^{II}(TCE-TTF^{•+})₂Zn^{II}(H₂O)₄](ClO₄)₆•2H₂O demonstrate that the organic radicals network do not contribute to the magnetism. Therefore, for **2** and **3** the Curie constant is proportional to the manganese amount, $\alpha = x + y$, with x and y defined in the chemical formula [Mn_xZn_{1-x}(TCE-TTF^{•+})₂Mn_yZn_{1-y}(H₂O)₄](ClO₄)₆•2H₂O

$$\chi_M = \frac{C}{T} = \frac{N\beta^2}{3kT} \alpha g^2 S(S+1)$$

with χ_M the magnetic molar susceptibility, the other symbols have their usual meaning, for Mn^{II} g = 2.00 and S = 5/2. The best agreement with Curie law is obtained with $\alpha = 0.209(1)$ for **3** and $\alpha = 1.57(1)$ for **2**. These values concord in a satisfactory manner with single crystal X-ray diffraction analysis and EDS: for **3** $\alpha = 0.18 + 0.12 = 0.3$ from X-rays and EDS and for **2** $\alpha = 0.92 + 0.70 = 1.62$ from X-rays (1.56 from EDS). There are two different octahedral crystallographic sites M(1) and M(2) with two different environments, however we cannot differentiate these two sites from the magnetization point of view and we obtain only the overall contribution.

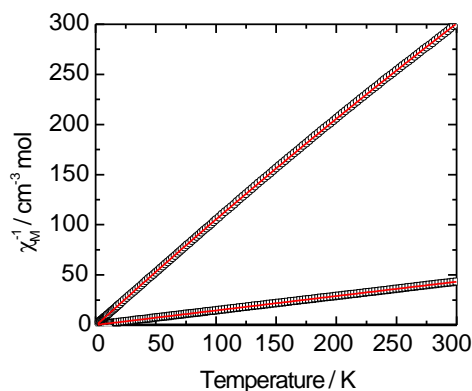


FIGURE 4. Thermal variation of χ_M^{-1} for compounds **2** (white squares) and **3** (white circles) with the best fitted curves with Curie law (full lines).

Compound [(TCE-TTF)Ag₃(CF₃SO₃)₃]•CH₃OH (4)

The silver containing compound was obtained by co-crystallization of 15 mg of the organic donor TCE-TTF and 50 mg of silver triflate Ag(CF₃SO₃) dissolved in 10 mL of a mixture CH₂Cl₂/MeOH 3/1. Suitable crystals for X-ray diffraction were obtained by slow evaporation after one week at 20°C. This compound crystallize in the centrosymmetric P-1 space group, crystallographic data are given in Table 3. The asymmetric unit is built up from one neutral TCE-TTF molecule, three CF₃SO₃⁻ and three Ag⁺ ions, all in general position. Each triflate anion is coordinated to silver ions by oxygen atoms of SO₃ fragments. The O9 atom of the first triflate anion is bridging two silver ions Ag2 and Ag1. The second triflate ion act as μ₃(η₂,η₁): O2 is η₂ bridging Ag2 and Ag1, and O3 is coordinated to Ag3. The third triflate ion is μ₂(η₁,η₁): O4 coordinates Ag3 and O5 coordinates Ag1. The whole packing consists of a neutral trimetallic edifice [Ag₃(CF₃SO₃)₃] depicted in Figure 5-a.

The four cyanoethylthio arms of the TCE-TTF molecule lie onto the same side of the plane defined by the TTF skeleton (cis type). This molecule is bound to silver ions by both sulphur and nitrogen atoms from cyanoethylthio groups. Each sulphur atoms of the cyanoethylthio arms is bound to silver cations: Ag1 is chelated with the sulphur atoms S7, S8 belonging to two arms from one side of the molecule, on the other side of the molecule, symmetrically, the remaining two sulphur atoms S1, S2 coordinate the silver ion Ag2. These bounds point out the high affinity between silver and sulphur atoms. Only one of the four nitrogen atoms of the molecule (N3) is not coordinated, the three other nitrogen atoms possess μ₁ coordination mode with silver: Ag3 is bridging N1 and N2 whereas Ag2 is bounding N5 (see Figure 5-b).

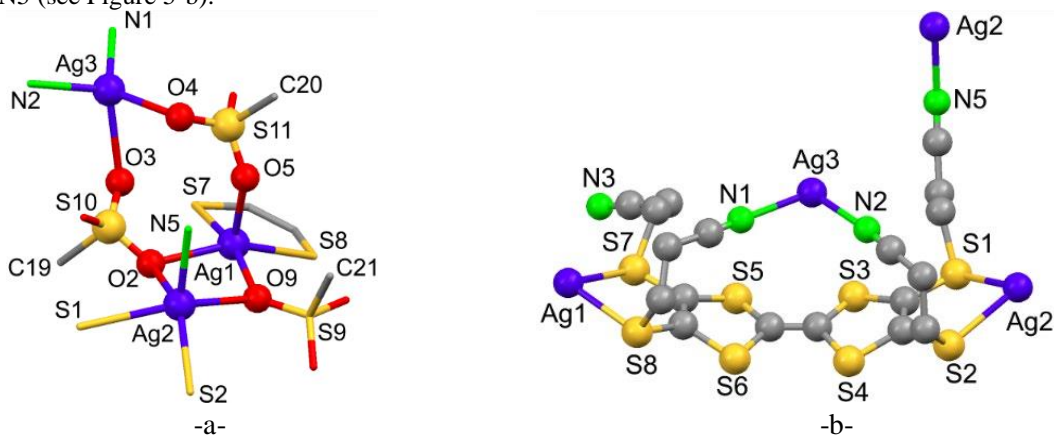


FIGURE 5. -a- Detail of the coordination sphere of trinuclear arrangement showing triflate anions. -b- detail of a TCE-TTF donor molecule and all coordinated silver cations with labelling scheme.

Each TCE-TTF molecule is coordinated to Ag1, Ag2 and Ag3, each silver belong to three different [Ag₃(CF₃SO₃)₃] blocks. On one side, -S7-C-C-S8- is chelating Ag1 cation from one trimetallic block, on the other side, -S1-C-C-S2- is chelating Ag2 cation from another block. TCE-TTF molecules and [Ag₃(CF₃SO₃)₃] blocs alternates along [2 0 -2] direction and form infinite {Ag1-TCE-TTF-Ag2}_n chains. Two parallel {Ag1-TCE-TTF-Ag2}_n chains are staggered rows such as the N5 atom from TCE-TTF coordinates the Ag3 cation from the closest neighbouring chain (see Figure 4-b). It form double chain which look like a ladder with {Ag1-TCE-TTF-Ag2}_n chains as the uprights and cyanoethylthyo arm S1-C-C-N5 as the main rungs (see top of Figure 5).

The TTF skeleton of one TCE-TTF molecule is stacked to [Ag₃(CF₃SO₃)₃] trimetallic molecule belonging to another double chain (Ag1...S6 = 3.253(2) Å) such as the external part of donor molecules from two adjacent double chains are able to interact thanks to short S...C contacts: S2...C1 = 3.354(6) Å; S8...C5 = 3.438(7) Å. (see Figure 5). Thanks to these short contacts, one can consider this polymer as a 2-D polymeric network.

Compound [(TCE-TTF^{•+})Zn(H₂O)_{3.2}(HClC-CHCl)_{0.8}](ReO₄)₃ (5)

The compound was obtained by electrocrystallisation technique. 100 mg of [(C₄H₉)₄N]ReO₄ and 30 mg of Zn(hfac)₂•xH₂O were dissolved in 20 mL of a mixture (benzene/tetrachloromethane/dichloromethane 1/1/1) and distributed in a two compartments U-shaped cell. 5 mg, (9.10⁻³ mmol) of TCE-TTF was added in the anodic compartment and a constant current of 0.5 μA was applied between two platinum wire electrodes. After two months

at 20°C, crystals appear in which zinc was de-coordinated from hfac⁻ ligands and μ_1 bounded to two nitrogen belonging to two TCE-TTF, to water molecules and to 1,2-dichloroethane molecule. It is known that compound containing hydrated zinc, in the presence of carbon tetrachloride, lead to the reduction of the chloride solvent as chloroform, methylene, chloride, methyl chloride, methane, and acetylene. The methylene chloride reduction, yield to traces of cis and trans-1,2-dichloroethene (DCE) [19] C–Cl bond cleavage of CH₂Cl₂ by the zinc^{II} complex, is also reported [20]. This compound crystallizes in the centrosymmetric P2₁/c space group, crystallographic data are given in Table 3.

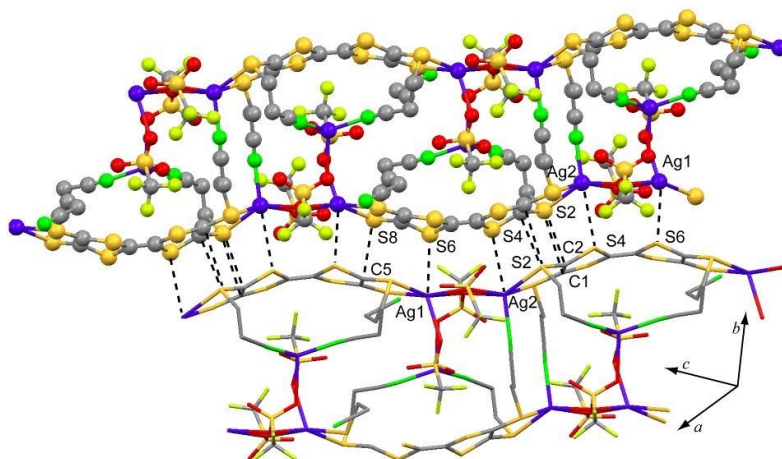


FIGURE 6 Detail of one double chain (ball and sticks) interacting with another double chain (capped sticks) thanks to short Ag \cdots S and C \cdots S contacts.

TABLE 3. Crystal data and structure refinement parameters for compounds **4** and **5**.

| Compound | 4 | 5 |
|--|---|--|
| Formula | C ₂₂ H ₂₀ Ag ₃ F ₉ N ₄ O ₁₀ S ₁₁ | C _{19.1} H _{18.2} Cl _{1.1} N ₄ O _{14.9} Re ₃ S ₈ Zn |
| Formula weight | 1347.69 | 1461.62 |
| Crystal system | Triclinic | Monoclinic |
| Space group | P-1 | P 2 ₁ /n |
| a/Å | 10.8627(4) | 16.6085(6) |
| b/Å | 12.4443(5) | 10.0688(2) |
| c/Å | 16.2872(6) | 24.5229(9) |
| α /° | 98.017(2) | 90. |
| β /° | 107.376(2) | 106.422(2) |
| γ /° | 91.823(2) | 90. |
| V/Å ³ | 2074.38(14) | 3933.6(2) |
| Z | 2 | 4 |
| Dc/g.cm ⁻³ | 2.158 | 2.468 |
| F(000) | 1316 | 2727 |
| μ (Mo-K α)/mm ⁻¹ | 2.050 | 10.368 |
| Total reflections | 16755 | 15144 |
| Unique reflections | 9490 | 8068 |
| I > 2 σ (I) | 5105 | 4452 |
| No. of parameters | 534 | 507 |
| GOF on F ² | 1.032 | 1.027 |
| R1 ^a | 0.0512 | 0.0556 |
| ω R2 ^b | 0.1226 | 0.1456 |
| $\Delta\rho_{\max}/\Delta\rho_{\min}/\text{e.}\text{\AA}^{-3}$ | 0.820 / -1.328 | 1.431 / -2.143 |

$$a R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad b \omega R_2 = \left\{ \frac{\sum [\omega(F_o^2 - F_c^2)^2]}{\sum [\omega(F_o^2)^2]} \right\}^{1/2}.$$

All the atoms of the asymmetric unit are in general position; it contains one TCE-TTF^{•+} radical, three ReO₄⁻ anions and one Zn^{II} ion surrounded with water molecules and 1,2-dichloroethane. Re2 atom is disordered in two positions Re2A and Re2B. The zinc cation is lying into an octahedral coordination sphere, two nitrogen atoms N1 and N4 in

trans position, two oxygen O1S and O2S from water molecules and two oxygen O3S and O4S from water molecules disordered with two chlorine C11S and C12S from 1,2 dichloroethane molecule (see Figure 6). Calculated occupation factors yield to ca. 45% of water molecules and 55% of dichloroethane. Bonds distances and angles involved in Zn coordination sphere are given in Table 4, the shorter distances correspond to the Zn-O contacts involving the non-disordered water molecules. Zn-O3S/C11S and Zn-O4S/C12S are close to 2.10 Å, and the angle C11-Zn-Cl2 of 79.0(3)° is consistent with the chelating dichloroethane molecule.

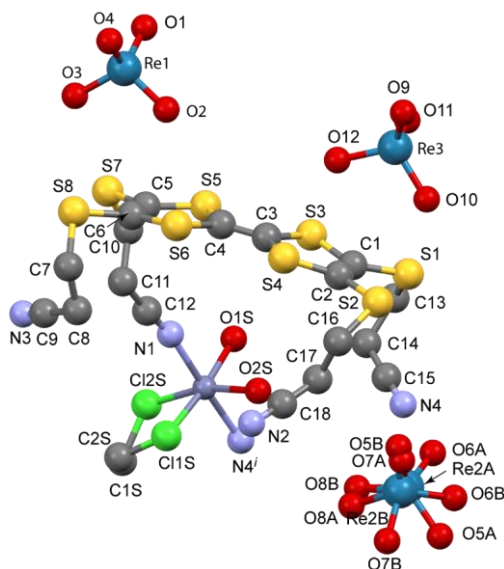


FIGURE 7. Drawing of $[(\text{TCE-TTF}^{\bullet+})\text{Zn}(\text{H}_2\text{O})_{3.2}(\text{HCIC-CHCl})_{0.8}](\text{ReO}_4)_3$ (**5**) with labelling scheme.

TABLE 4. Selected bond lengths [Å] and angles [°] for (**5**). C11S and O3S; C12S and O4S are lying into the same position

| | | | |
|-------------------------|-----------|-------------------------|-----------|
| N1-Zn | 2.084(13) | N4-Zn ⁱ | 2.183(14) |
| Zn-O2S | 2.017(10) | Zn-O1S | 2.062(10) |
| Zn-O4S/C12S | 2.095(8) | Zn-O3S/C11S | 2.114(8) |
| O2S-Zn-O1S | 97.1(4) | O2S-Zn-N1 | 93.9(5) |
| O1S-Zn-N1 | 90.1(5) | O2S-Zn-O4S/C12S | 166.2(4) |
| O1S-Zn-O4S/C12S | 94.7(4) | N1-Zn-O4S/C12S | 93.1(5) |
| O1S-Zn-O3S/C11S | 173.5(4) | N1-Zn-O3S/C11S | 88.5(5) |
| O4S/C12S-Zn-O3S/C11S | 79.0(3) | O2S-Zn-O3S/C11S | 89.4(4) |
| O2S-Zn-N4 ⁱⁱ | 86.3(5) | O1S-Zn-N4 ⁱⁱ | 86.6(5) |
| N1-Zn-N4 ⁱⁱ | 176.7(6) | | |

Symmetry code *i*: 1/2-x, y+1/2, 1/2-z; *ii*: 1/2-x, y-1/2, 1/2-z

Each TCE-TTF^{•+} radical is connected to two zinc cations, whereas each zinc cation is bridging two TCE-TTF^{•+} thanks to apical coordination N4-Zn-N1 bridges (see Figure 7-a-). These two TCE-TTF^{•+} radicals are crystallographically linked by a 2₁ axis, and a chiral helix wrap along the crystallographic b axis. The elongated molecular axis of TCE-TTF is perpendicular to the helix axis, a view along crystallographic b axis, is given in Figure 7b. Helixes are connected along c axis thanks to centrosymmetric short contacts involving sulphur atoms S1ⁱ•••S1^{ix} = 3.201(7) and S2ⁱⁱ•••S2^{ix} = 3.546(7) Å. Along a axis, planes of helixes are connected thanks to contacts S5•••S6^{xiii} = 3.410(5) Å (see Figure 9)

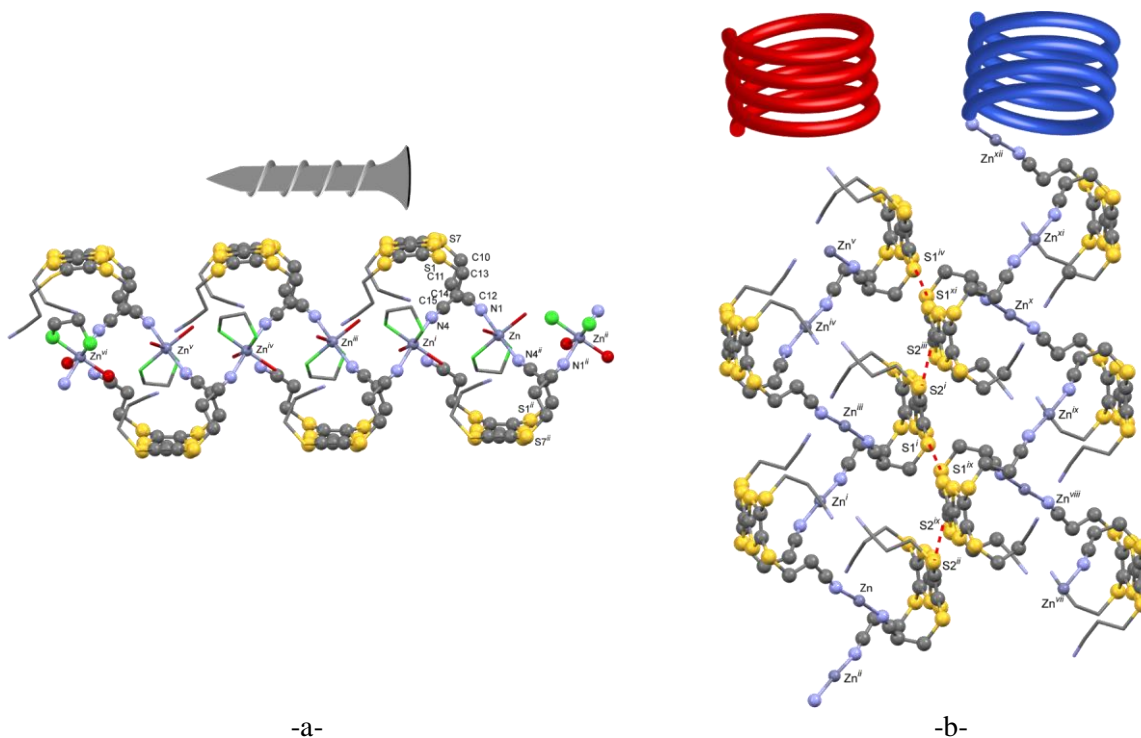


FIGURE 8. -a- helix chain along b axis for (5); -b- Close right-handed and left-handed helix with symmetries codes for both -a- and -b- drawings i: $1/2-x, y+1/2, 1/2-z$; ii: $1/2-x, y-1/2, 1/2-z$; iii: $x, y+1, z$; iv: $1/2-x, y+3/2, 1/2-z$; v: $x, y+2, z$; vi: $1/2-x, y+5/2, 1/2-z$; vii: $x-1/2, -y-3/2, z-1/2$; viii: $-x, -1-y, -z$; ix: $x-1/2, -1/2-y, z-1/2$; x: $-x, -y, -z$; xi: $x-1/2, 1/2-y, z-1/2$; xii: $-x, 1-y, -z$

Contacts shorter the van der Waals sum radii involving ReO_4^- anions and TCE-TTF are observed: $\text{S4}\cdots\text{O7B}^{\text{ii}} = 3.163(81) \text{ \AA}$ and $\text{S4}\cdots\text{O12}^{\text{xiii}} = 3.181(16) \text{ \AA}$. Nitrogen atoms do not involve short contact, the shortest contact ($\text{N2}\cdots\text{O5B} = 3.22(6) \text{ \AA}$) being 0.16 \AA longer the corresponding van der Waals radii sum. Due to the centrosymmetric $\text{P2}_1/\text{n}$ space group, compound (5) is not chiral as the helix chirality right-handed and left-handed alternates in the compound.

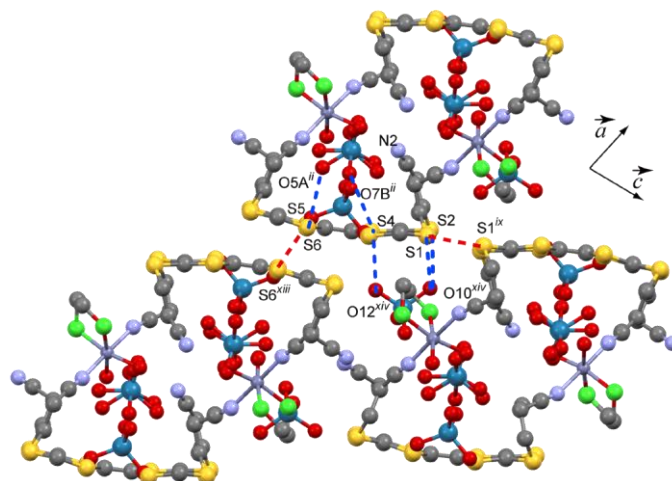


FIGURE 8. Three helix chains viewed along b axis for (5) with intermolecular S...S and S...O contacts shorter the van der Waals distances. Symmetries used ii: $1/2-x, y-1/2, 1/2-z$; ix: $x-1/2, -1/2-y, z-1/2$; xiii: $3/2-x, y-1/2, 1/2-z$; xiv: $1/2+x, -1/2-y, 1/2+z$.

CONCLUSION

TCE-TTF revealed its ability to grow as polymers once associated to transition ions. Three different polymeric phases were characterized. Compounds **1-3** are isostructural heterometallic polymers of TCE-TTF^{•+} radicals, and possess two crystallographically independent metal sites. It was shown that from starting reagents composed of a mixture of two transition metals with different radius, the polymer mainly contains the larger metallic ion; furthermore, the six-nitrogen octahedral coordination sphere is predominantly fulfilled with the larger ion. Magnetic measurements performed for **2** and **3** revealed that the Mn/Zn metal stoichiometry is coherent with those observed with EDS and X-rays characterizations. Compound **4** is built with neutral TCE-TTF and neutral silver-triflate, it form 1-D double chains strongly interacting to give rise pseudo-2D polymers. Compound **5** revealed axially chiral helical motifs of neutral TCE-TTF molecules coordinated to zinc cation. During this crystallization the reduction of the chlorine solvent was observed, and dichloroethane was in-situ obtained and coordinated to Zinc ion.

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