

# TETRATHIAFULVALENE-OXAZOLINES (TTF-OX) AND DERIVATIVES: VALUABLE PRECURSORS FOR CHIRAL CONDUCTORS AND ELECTROACTIVE COMPLEXES

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Received December 17, 2008

The synthesis and structural characterization of racemic and enantiopure tetrathiafulvalene-oxazolines (TTF-OX) derivatives, with an emphasis on several key features, are reviewed. These compounds can serve as precursors for conducting chiral materials, but also as electroactive ligands for transition metal complexes. Crystalline conducting molecular materials have been obtained upon electrocrystallization of some of the donors, such as the first complete series of mixed-valence metallic salts based on chiral tetrathiafulvalenes, bearing the (*R*)-, (*S*)-, or racemic ( $\pm$ )-methyl-oxazoline heterocycle and the  $\text{AsF}_6^-$  monoanion. Transition metal complexes containing electroactive TTF-OX ligands have been prepared as well. Palladium and iridium complexes containing TTF-phosphino-oxazoline (TTF-PHOX) ligands have been applied in two homogeneous catalytic processes.

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## INTRODUCTION

The introduction of chirality in conducting molecular materials based on tetrathiafulvalene (TTF) derivatives, a well known class of organosulfur electron donors extensively studied in the field of molecular conductors and superconductors,<sup>1</sup> receives currently a growing interest, motivated in particular by Rikken *et al.*'s recent reports of an electrical magnetochiral anisotropy effect in chiral carbon

nanotubes.<sup>2</sup> This effect is related to the interplay between the conductivity of a chiral conductor, measured under an applied magnetic field, and the handedness of the chiral compound. As a consequence, weak differences between the values of the conductivity of the opposite enantiomers, and also with respect to the racemic compound, can be possibly experimentally evidenced. In spite of the low magnitude of this effect, its interest in spintronics has been evoked.<sup>3</sup> This feature is in line

with the quest for multifunctional molecular materials, aiming at combining in the solid state at least two physical properties, such as conductivity and optical activity.<sup>4</sup> However, the question of whether the chirality influences the electrical properties of TTF based radical cation salts had been previously addressed by Dunitz and Wallis, but the lack of suitable enantiopure materials together with their racemic form did not allow deeper investigations.<sup>5</sup> Yet, structural differences between racemic and enantiomeric forms may occur, since enantiopure radical cation salts are expected to suffer less from structural disorder than the racemates, whose crystal structures might, in principle, accommodate enantiomers exchanging places. It is well established that structural disorder

can strongly influence the electronic conductivity in molecular conductors,<sup>6</sup> therefore the chirality can already intervene at this level. A straightforward strategy to introduce chirality within TTF based materials lies in the utilization of chiral TTF's as precursors for radical cation salts. The first examples of enantiopure TTF derivatives with the corresponding radical cation salts were described by Dunitz and Wallis,<sup>7</sup> and concerned in particular the derivative (*S,S,S,S*)-TM-BEDT-TTF. Furthermore, conducting salts of the donor DM-BEDT-TTF, either enantiopure (*S,S*) or racemic, have been also described.<sup>8</sup> Since then several series of chiral TTF's were synthesized, most of them featuring a functionalized BEDT-TTF (BEDT-TTF = bis(ethylenedithio)-tetrathiafulvalene) skeleton.<sup>9</sup>

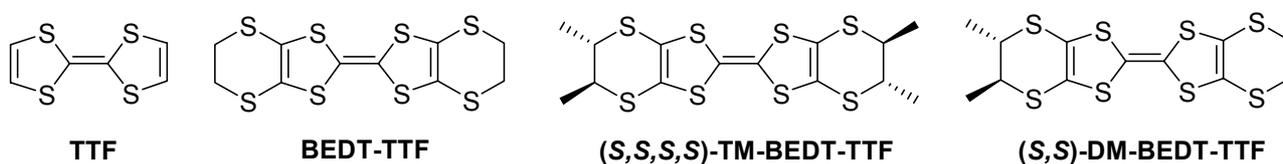


Chart 1 – Examples of tetrathiafulvalenes.

In other derivatives the chirality has been introduced through the bias of a binaphthyl fragment,<sup>10</sup> or an oxazoline ring.<sup>11</sup> These latter are TTF-oxazoline derivatives and have been only used as ligands for the nucleophilic allylic substitution reaction, with mediocre results in term of activity and selectivity. The complementary strategy, consisting in the utilisation of an achiral donor in combination with an enantiopure anion, has been also occasionally exploited, such as in the

semiconducting salt of BEDT-TTF with (*L*)-tartrate antimonate [Sb<sub>2</sub>(*L*-tart)<sub>2</sub>]<sup>2-</sup>.<sup>12</sup> However, throughout all the examples described so far, there was no complete series comprising both enantiomers and also the racemic form in order to directly compare their physical properties. Recently we have described the straightforward synthesis of chiral EDT-TTF-oxazolines together with phosphino<sup>13</sup> and thioether<sup>14</sup> derivatives (Chart 2).

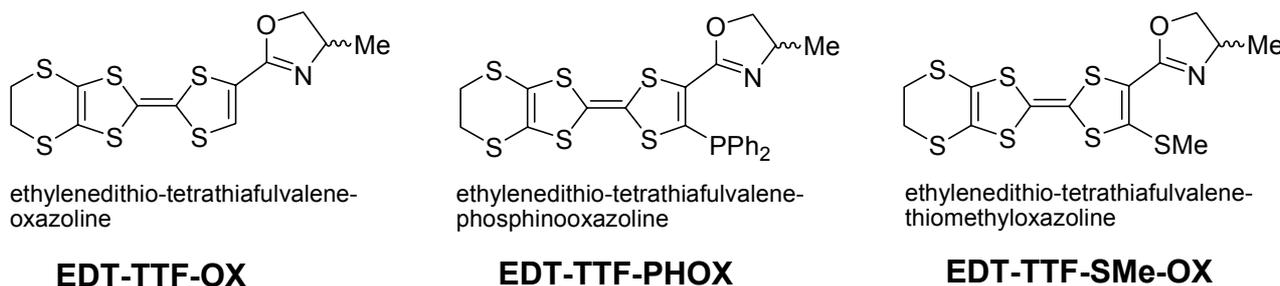


Chart 2 – Chiral TTF-oxazolines and derivatives.

By the synthesis of these derivatives our goal was twofold: first, we wanted to access a new family of chiral donors to be used as precursors for chiral molecular materials; secondly, we envisaged to use these electroactive oxazolines as electroactive ligands for transition metal complexes. In this respect, the association of the

redox active TTF unit with potentially coordinating fragments is particularly appealing in the perspective of preparing electroactive transition metal complexes with interesting features. First, the electron density on the metallic centre could be tuned by the TTF oxidation state, as demonstrated in a series of TTF-phosphine metal-carbonyl



and only a weak folding about S...S hinges. TTF and oxazoline units are coplanar, with the corresponding dihedral angle amounting at  $7.31(51)^\circ$ , an important feature in view of obtaining radical cation salts based on EDT-TTF-Me-OX. The enantiopure isopropyl-oxazolines **4** are isostructural and

crystallize in the non-centrosymmetric orthorhombic space group  $P2_12_12_1$ , with one independent molecule in the unit cell. The conformation in the solid state is once again the same *s-trans* one (Figure 1).<sup>13</sup>

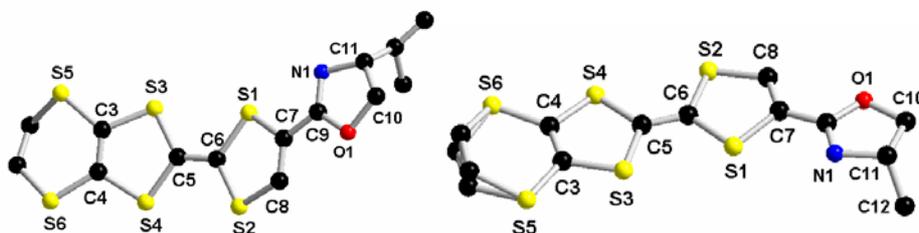
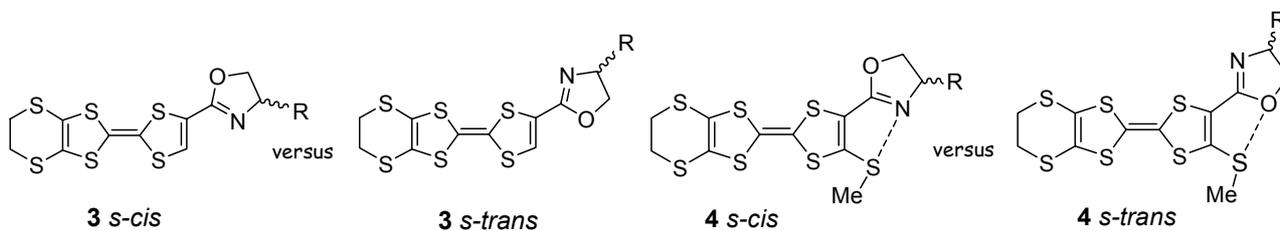


Fig. 1 – Crystalline structures of **3a** (*S*) (left) and **3b** (*R*) (right). Hydrogen atoms have been omitted.

However, the packing of the molecules is completely different between the Me-OX **3a** and *i*Pr-OX **3b** derivatives. Thus, the change of the substituent induced substantial modifications in the solid state organization, since molecules **3a** adopt a herring bone type arrangement, while molecules **3b** organize in the more classical head-to-tail dimers pattern (Figures 2). The shortest intermolecular S...S distances amount to 4.01 Å in the case of **3a** and 3.7 – 3.8 Å in the case of **3b**.

Suitable single crystals for X-ray diffraction studies have been also obtained for the donors EDT-TTF-SMe-OX **4a** and **4b**.<sup>14</sup> The enantiopure oxazolines **4a** (*R*) and **4a** (*S*) are isostructural, crystallizing both in the orthorhombic system, non-centrosymmetric space group  $P2_12_12_1$ , with one independent molecule in the unit cell, in general position.

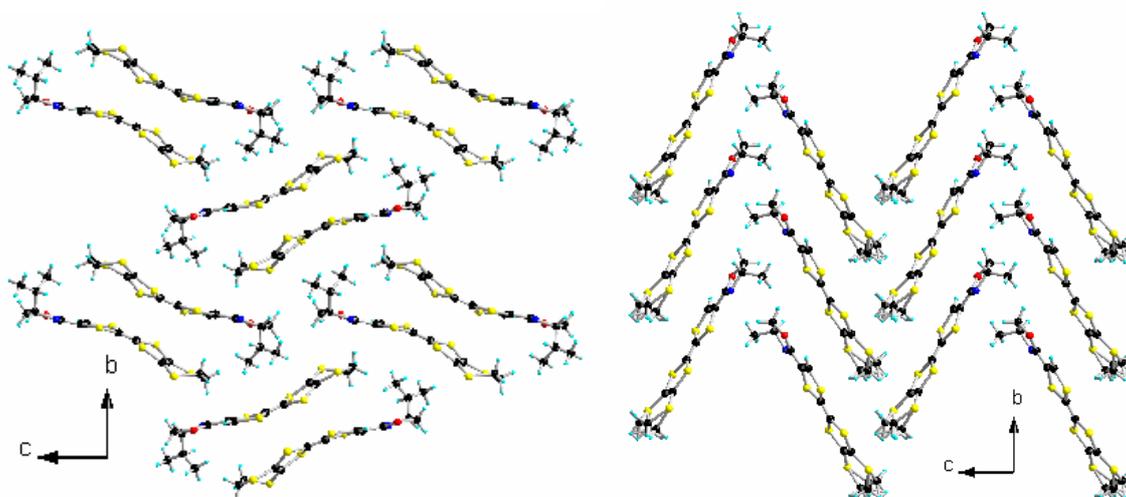


Fig. 2 – Packing diagrams of **3a** (*S*) (left) and **3b** (*R*) (right).

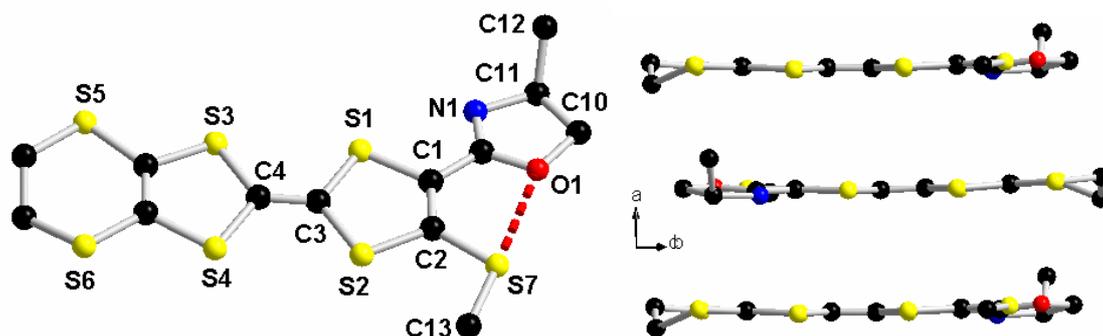


Fig. 3 – Structure of (*S*)-EDT-TTF-SMe-OX **4a**. Selected parameters: O(1)⋯S(7) 2.87 Å; angles (°): O(1)⋯S(7)–Me 176.2, torsion (°): TTF⋯OX 5.7, TTF⋯SMe 3.3. Hydrogen atoms have been omitted (left). Packing of molecules **4a** along the *a* direction (right).

The most striking feature in the solid state structures of **4a** is the establishment of a short intramolecular O(1)⋯S(7) contact at 2.87 Å (Figure 3). This distance is largely within the sum of the van der Waals radii of S and O atoms (3.32 Å), clearly indicating the establishment of a O⋯S 1,5-type nonbonded interaction, also characterized by the colinearity of the O⋯S–Me motif. The TTF-Oxazoline conformation is thus of *s-trans* type and the overall geometry of the donor molecule is flat. Intermolecular S⋯S distances in the stacks amount to 3.8 – 3.9 Å. Interestingly, the quasi-planarity of the molecules allows for the engagement of the SMe sulfur atom in rather short S⋯S intermolecular contacts, thus suggesting its possible participation in the electron delocalization in corresponding radical cation salts. Intramolecular bond lengths are typical for neutral TTF derivatives. Note however that theoretical calculations at DFT level

demonstrate that both conformations, *i.e.* *s-cis* and *s-trans*, are energy minima.<sup>14</sup>

### CHIRAL MOLECULAR METALS IN THE SERIES OF TTF-OXAZOLINES

Electrocrystallization of the series **3a** ( $\pm$ ), (*R*) and (*S*) in CH<sub>2</sub>Cl<sub>2</sub> solutions containing (*n*-Bu)<sub>4</sub>NAsF<sub>6</sub> as supporting electrolyte afforded black needles of salts formulated as [4]<sub>2</sub>AsF<sub>6</sub>. The racemic [( $\pm$ )-**4**]<sub>2</sub>AsF<sub>6</sub> salt crystallizes in the triclinic system, space group *P*-1 with the AsF<sub>6</sub><sup>-</sup> anion on an inversion centre, one donor molecule in general position in the unit cell and the oxazoline ring, almost coplanar with the TTF core but *disordered* over two positions, corresponding to both *R* and *S* enantiomers on the same site, one as *s-cis* and the other as *s-trans* conformers (Figure 4).

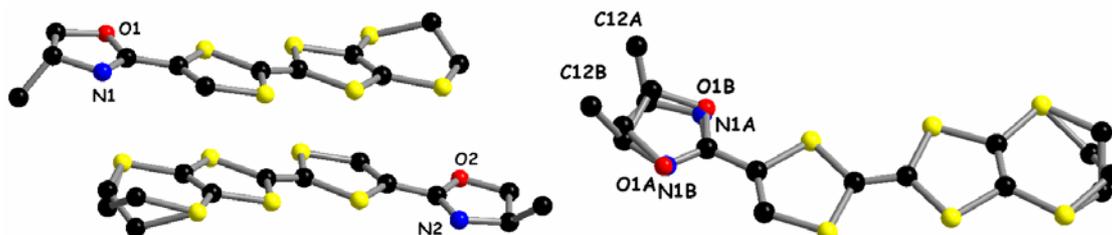


Fig. 4 – Crystalline structures of [( $\pm$ )-**3a**]<sub>2</sub>AsF<sub>6</sub> (left) and [(*R*)-**3a**]<sub>2</sub>AsF<sub>6</sub> (right).

Enantiopure [(*R*)-**3a**]<sub>2</sub>AsF<sub>6</sub> and [(*S*)-**3a**]<sub>2</sub>AsF<sub>6</sub> are isostructural and crystallize in the chiral space group *P*1 with one anion and two crystallographically independent donor molecules as *s-cis* and *s-trans* conformers respectively, which also differ by the disorder of the ethylene moiety observed only within the *s-trans* conformer. It is thus important to note the difference between the racemic salt, with a structural disorder, and the enantiopure counterparts who are perfectly ordered as far as the oxazoline rings are

concerned. In the solid state, the racemic and enantiopure salts adopt closely related layered structures, with stacks of donor molecules along *b*, interacting side-by-side along *a*. Within each stack, the molecules alternate in a head-to-tail manner, with bond-over-ring overlaps. The donor slabs thus adopt the so-called  $\beta$ -type structural motif (Figure 5a), as encountered for example in the superconducting  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> salt.<sup>22</sup> Single crystal conductivity measurements have been performed on all the three

salts, showing metallic character at room temperature (Figure 5b) with  $\sigma_{RT} \approx 100 \text{ S cm}^{-1}$  in the pure enantiomers while the room temperature conductivity of the ( $\pm$ ) salt is one order of magnitude lower ( $\sigma_{RT} \approx$

$10 \text{ S cm}^{-1}$ ). Upon lowering the temperature the resistivity shows a broad minimum around 230 K followed by a localized regime.<sup>23</sup>

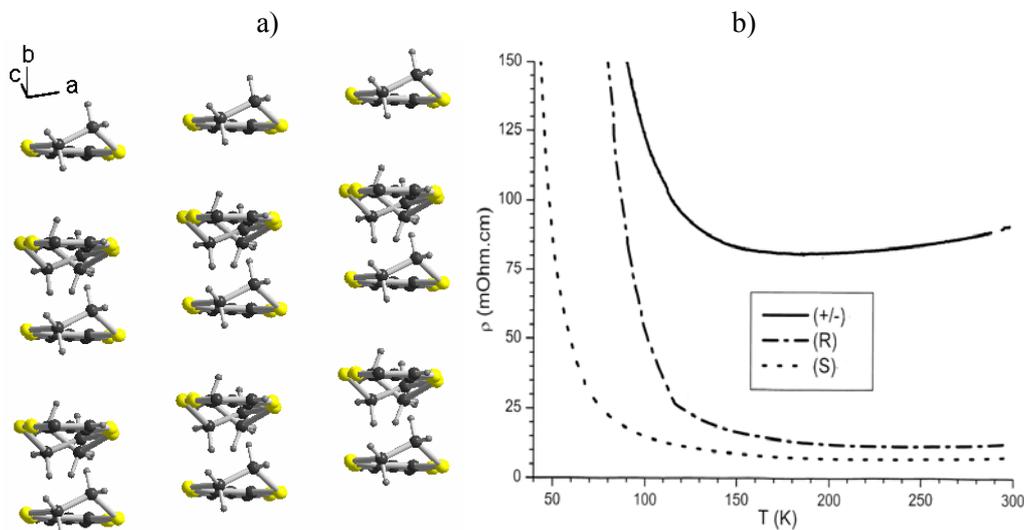


Fig. 5 – The organic slab in  $[(R)\text{-}\mathbf{3a}]_2\text{AsF}_6$ , viewed along the TTF long axis. Oxazoline rings have been omitted for clarity (a). Temperature dependence of the resistivity for  $[(R)\text{-}\mathbf{3a}]_2\text{AsF}_6$ ,  $[(S)\text{-}\mathbf{3a}]_2\text{AsF}_6$  and  $[(\pm)\text{-}\mathbf{3a}]_2\text{AsF}_6$  (b).

The conductivity of the racemic salt, with the additional source of disorder due to the presence of both *R* and *S* enantiomers on the same site, is approximately one order of magnitude weaker than the conductivity of the enantiopure salts, emphasizing the paramount role played by different disorder sources in the conductivity behavior of such cation radical salts. Indeed, despite closely related crystalline and electronic structures, the higher conductivity of pure enantiomers, lacking the structural disorder of the racemic mixture, demonstrates that this chiral donor route is very promising for the elaboration of other metallic salts, taking into account that the substituent on the oxazoline ring or the nature of the counter ion can be easily modified.

#### COORDINATION CHEMISTRY WITH TTF-OXAZOLINES BASED LIGANDS

A series of paramagnetic complexes  $[\mathbf{3a}]\text{Cu}^{\text{II}}(\text{hfac})_2$  has been conventionally prepared, by stirring a mixture of the ligands  $\mathbf{3a}$  with the appropriate amount of  $[\text{Cu}(\text{hfac})_2]$  precursor in a non-coordinating solvent, *i.e.*  $\text{CH}_2\text{Cl}_2$ -hexane mixture. Suitable single crystals for X-ray analysis for the three compounds were grown upon slow evaporation of the solutions. The racemic complex crystallizes in the triclinic system, centrosymmetric

space group  $P\bar{1}$ , with one independent molecule in the asymmetric unit cell in general position, whereas its enantiopure counterparts crystallize in the triclinic system, chiral space group  $P1$ . In the structure of the complex  $(\pm)\text{-}[\mathbf{3a}]\text{Cu}^{\text{II}}(\text{hfac})_2$  (Figure 6) one can observe the pentacoordination of the Cu(II) centre in a slightly distorted square pyramid, with the basal plane formed by three oxygen atoms (O2, O3 and O4) and the oxazoline nitrogen atom N1, while the oxygen atom O5 is located in the apical position, with a longer Cu1---O5 distance amounting to 2.192(4) Å. The equatorial Cu---O and Cu---N distances range between 1.937(4) – 1.976(4) Å. Interestingly, the sulfur atom S1 of the TTF core is semi-coordinated in the second apical position at a much longer distance (Cu1---S1 = 2.949(5) Å).<sup>24</sup>

In the crystalline structures of the enantiopure complexes (*R*) and (*S*) there is no occupational disorder at the chiral carbon atoms C11 and C33. The system accommodates two independent molecules of complex in the unit cell, in general positions, corresponding each other through a *pseudo* inversion centre. The difference between the two molecules relies on the enantiomeric related configurations around the coordinated metallic centre, if one considers a distorted coordination geometry by taking into account the secondary Cu---S<sub>TTF</sub> interaction, ranging between 2.91 – 2.97 Å,

a typical distance for a semi-coordination. Accordingly, the two molecules are ( $\Delta,S$ ) and ( $\Delta,S$ ) diastereoisomers for ( $S$ )-[**3a**]Cu<sup>II</sup>(hfac)<sub>2</sub> (Figure 6) and ( $\Delta,R$ ) and ( $\Delta,R$ ) diastereoisomers for

( $R$ )-[**3a**]Cu<sup>II</sup>(hfac)<sub>2</sub>. Besides, the coordination pattern around the metallic center parallels the one observed in the racemic compound.

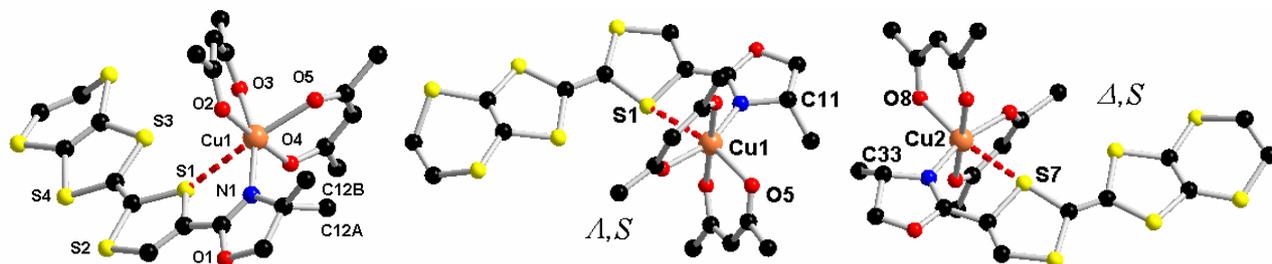


Fig. 6 – Crystalline structure of ( $\pm$ )-[**3a**]Cu<sup>II</sup>(hfac)<sub>2</sub>, with an emphasis on the coordination geometry around the Cu(II) centre. Fluorine and hydrogen atoms have been omitted for clarity (left). Crystalline structure of ( $S$ )-[**3a**]Cu<sup>II</sup>(hfac)<sub>2</sub>, showing the formation of two diastereoisomers (right).

The observation of this Cu<sup>II</sup>---S<sub>TTF</sub> secondary coordination in the crystal structures of [**3a**]Cu<sup>II</sup>(hfac)<sub>2</sub> prompted us to react the same [Cu(hfac)<sub>2</sub>] fragment with the potentially chelating TTF derivatives EDT-TTF-SMe-OX **4a**. Of particular interest in our case would be the competition between the Cu---S<sub>TTF</sub> and Cu---SMe interactions, knowing that the Cu(II) centre can easily adapt its coordination sphere to a penta- or a

hexa-coordination. The complex ( $\pm$ )-[**4a**]Cu<sup>II</sup>(hfac)<sub>2</sub> crystallizes in the monoclinic system, space group  $P2_1/c$ , with one independent molecule in the unit cell. Surprisingly, the metallic centre prefers once again in the solid state a pentacoordination in a distorted square pyramid geometry, with a weak Cu---S<sub>TTF</sub> apical interaction (Cu1 – S1 = 3.039(2) Å) (Figure 7).

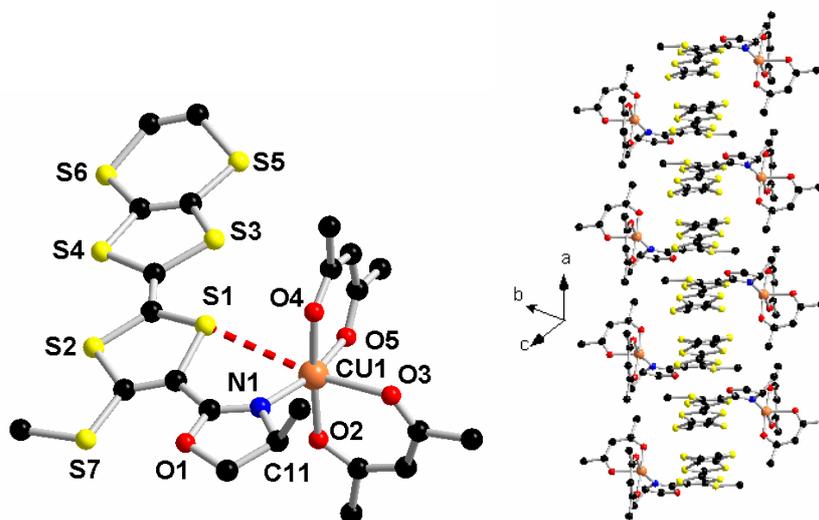


Fig. 7 – Crystalline structure of ( $\pm$ )-[**4a**]Cu<sup>II</sup>(hfac)<sub>2</sub>, with an emphasis on the coordination geometry around the Cu(II) centre. Fluorine and hydrogen atoms have been omitted for clarity (left). Stack of TTFs (right).

Note that in this case we did not identify any disorder at the chiral centre C11, but again some of the fluorine atoms are disordered. Quite uniform TTF one-dimensional TTF stacks are established along the  $a$  axis (Figure 7), with S---S intermolecular distances of 3.7 Å, at the van der Waals limit. As in the previous complexes, the

Cu(II) centres are practically isolated each other, when considering the shortest Cu---Cu distance of 9.38 Å. Nevertheless, we investigated the magnetic behavior for crystalline samples of ( $S$ )-[**3a**]Cu<sup>II</sup>(hfac)<sub>2</sub> and ( $\pm$ )-[**4a**]Cu<sup>II</sup>(hfac)<sub>2</sub>. In both cases the variation of the magnetic susceptibility with the temperature follows a Curie law for a spin

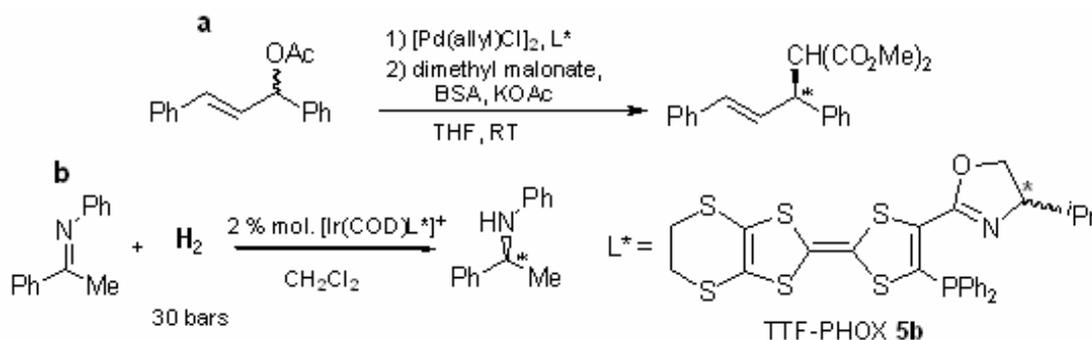
$S = \frac{1}{2}$ , as demonstrated by the constant value ( $\approx 0.4 \text{ emu.K.mol}^{-1}$ ) of the product  $\chi T$  ( $\chi$  = molar magnetic susceptibility) in the whole range of temperature. These results are in agreement with isolated paramagnetic Cu(II) centers with  $S = \frac{1}{2}$ , a likely consequence of the quite long distance between the closest neighboring Cu(II) ions within the crystal. Cyclic voltammetry measurements for these complexes show the classical two reversible one-electron oxidation processes at 0.64 and 1.12 V vs. SCE, corresponding to the formation of TTF radical cation and then dication. These results are promising in the perspective of the preparation of molecular materials provided simultaneously with conducting and magnetic properties.

### TTF-PHOSPHINO-OXAZOLINES AS ELECTROACTIVE LIGANDS FOR THE HOMOGENEOUS CATALYSIS

The primary objectives related to the synthesis of the TTF-phosphino-oxazolines (TTF-PHOX) **5a-b** concerned their utilization in catalytic reactions for which phosphino-oxazoline ligands proved their efficiency. Besides catalytic activity and selectivity, our interest in the study of these ligands is also to investigate whether the oxidation

state of TTF has an influence on the catalytic process, in order to achieve a redox modulation of the catalytic reaction.<sup>25</sup> In principle one can consider that the electronic density and the coordination sphere of a metallic center are likely to vary with the oxidation state of the electroactive ligand if the electronic communication between the metal and the ligand is efficient. We have first selected two catalytic reactions, namely the nucleophilic allylic substitution, also known as the Tsuji-Trost reaction,<sup>26</sup> and the hydrogenation of imines in order to test our TTF-PHOX ligands (Scheme 2). As expected, the best results were obtained with the isopropyl substituted oxazolines **5b**.

For the Tsuji-Trost reaction, we have chosen the standard substrate 1,3-diphenyl-propenyl-acetate, the Pd(II) complex  $[\text{Pd}(\pi\text{-allyl})\text{Cl}]_2$  as catalyst precursor and the dimethyl malonate as source for the malonate anion.<sup>27</sup> For this reaction our ligands **5b** show modest activity, with about 20% conversion, yet the enantiomeric excesses (*ee*) reach 85-90%. In a second series of tests, the oxidized ligands have been used, without any major difference with respect to the neutral ligands. Note however that in the reaction conditions we cannot rule out the possibility of a reduction of the TTF radical cation back to the neutral TTF.



Scheme 2 – Asymmetric allylic alkylation (a) and hydrogenation of imines (b) with the ligands TTF-PHOX **5b**.

The second reaction we have investigated is the reductive enantioselective hydrogenation of imines, which is a very important process for the industry, since the resulting compounds are chiral amines, often encountered in the structure of biologically active molecules.<sup>27</sup> Among the most efficient catalysts for this reaction stand the Ir(I) based complexes containing chiral bis(phosphines) or P,N ligands. During the catalytic process one can disclose an oxidative addition of dihydrogen to provide a bis(hydrido)  $\text{H}_2\text{Ir(III)}$  complex, then the coordination of the imine followed by a hydrogen

transfer, to finish with the reductive elimination of the amine. We have thus synthesized the cationic complexes  $[(\mathbf{5b})\text{Ir}(\text{COD})]^+$  (COD = cyclooctadiene), either with the anion  $\text{PF}_6^-$  or with the  $\text{BArF}^-$  ( $\text{BArF}^- = \text{tetrakis}[3,5\text{-bis}(\text{trifluoromethyl})\text{-phenyl}]\text{borate}$ ). The starting imine was the N-phenyl-benzylmethyl-imine.<sup>28</sup> This time our ligands proved to be very active, since the conversions are quantitative after a few hours, with *ee*'s attaining 70% in the case of the non-coordinating anion  $\text{BArF}^-$ . Much lower

conversions and *ee*'s were observed with the oxidized ligands. In conclusion, it is certain that the TTF-PHOX ligands present an interesting potential in catalysis, yet the influence of the oxidation state of TTF requires deeper spectroscopic and electrochemical investigations in order to establish the nature of the different species of the catalytic cycles.

## CONCLUSIONS

The synthesis of chiral TTF-oxazolines and derivatives allowed us to access a family of versatile compounds, useful as precursors for chiral conductors, but also as electroactive ligands for homogenous catalytic reactions and for paramagnetic coordination complexes. Thanks to the TTF-methyl-oxazolines precursors we have synthesized the first complete series of chiral molecular metals, in which we could evidence the role of the chirality in the conductivity properties through the bias of the structural crystalline disorder. Further investigations in the field of the multifunctional materials are on the way, aiming at emphasizing an electrical magneto-chiral effect in TTF based conductors. We have shown that the TTF-oxazolines and TTF-thiomethyl-oxazolines can act efficiently as ligands for paramagnetic metallic centers, as a first step towards the preparation of functional materials allying conductivity chirality and magnetism. Finally, a last facet of these derivatives concerns their interesting potential as electroactive ligands for diverse catalytic reactions, as we could demonstrate in the case of the nucleophilic allylic substitution and the hydrogenation of imines. Other reactions are under active investigation in our group.

*Acknowledgements:* The author would like to warmly acknowledge M. Fourmigué (Univ. Rennes 1, France), Dr. C. Réthoré and Dr. A. Madalan for their substantial contribution to this research. Many thanks also to E. Canadell (ICMAB, Barcelona, Spain.) for band structure calculations, P. Auban-Senzier (University Paris XI Orsay, France) for conductivity measurements, I. Suisse and F. Agbossou-Niedercorn (ENSCL Lille, France) for the catalytic reactions. This research work was supported by the CNRS, French Ministry of Education and Research (grant to C. Réthoré), and Région Pays de la Loire (grant to A. Madalan).

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