

Copper (II) and cobalt (II) complexes of chiral tetrathiafulvalene-oxazoline (TTF-OX) and tetrathiafulvalene-thiomethyl-oxazoline (TTF-SMe-OX) derivatives

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Abstract

Synthesis and single crystal X-ray structures of the first paramagnetic transition metal complexes containing chiral ethylenedithio-tetrathiafulvalene-oxazoline (EDT-TTF-OX) **1a–c** and ethylenedithio-tetrathiafulvalene-thiomethyl-oxazoline **2** (EDT-TTF-(SMe)OX) ligands based on copper (II) and cobalt (II) are described. The racemic [EDT-TTF-OX][Cu(hfac)₂] complex **3a** crystallizes in the triclinic centrosymmetric space group $P\bar{1}$, whereas the enantiopure counterparts **3b–c** crystallize in the triclinic non-centrosymmetric space group $P1$. Cu(II) adopts a distorted square pyramidal coordination geometry, a much weaker Cu··S_{TTF} interaction also being identified. The same coordination pattern around Cu(II) is observed in the complex [(*rac*)-EDT-TTF-(SMe)OX][Cu(hfac)₂] (**4**) in spite of the bidentate nature of the redox active ligand. DFT theoretical calculations afforded two equilibrium configurations for a corresponding model complex, in which the metal centre establishes secondary coordination either with one S_{TTF} or with the SMe group. The same ligand coordinates the cobalt (II) to afford the octahedral complex [(*rac*)-EDT-TTF-(SMe)OX][Co(hfac)₂] (**5**). In all these novel complexes, the paramagnetic centres are structurally and magnetically isolated. Cyclic voltammetry measurements show the stability of the radical cation species.

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1. Introduction

During the past decade, a lot of efforts have been devoted to the synthesis and coordination chemistry of ligands containing the tetrathiafulvalene (TTF) redox active unit. It is well known that TTF and derivatives reversibly oxidize in a one-electron process to afford stable radical cation species [1], eventually leading to mixed valence salts that can exhibit conducting or superconducting properties in the solid state [2]. 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 is eventually tuned by the TTF oxidation state, as demonstrated in a series of TTF-phosphine metal–carbonyl complexes [3]. Second, two or more TTF units can be assembled around the metal in a predefined manner, depending on the stereochemical preferences of the metal ion and the number of free coordination sites, thus allowing an easy access to different electroactive molecular building-blocks [4]. Yet, one of the most interesting situations occurs when the coordinated metal is paramagnetic, since magnetic and conducting properties could coexist or interplay in the solid state, leading to bifunctional materials, a trend of much current interest in

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the field of molecular materials [5]. Numerous TTF based ligands capable of coordinating transition metals have been described, such as thioethers [6], phosphines [7], or pyridines and derivatives [8]. Some corresponding transition metal complexes, in which the TTF units are either neutral [9] or, in a couple of cases, oxidized [10], have also been prepared. To our knowledge, all the complexes but one [11] described so far and structurally characterized contained only achiral TTF based ligands. This feature is certainly due to the lack of appropriate chiral ligands, even though chiral TTF derivatives have been known since long [12]. Therefore, in line with the increasing interest around the multifunctional materials [5], we were interested in the synthesis of complexes based on chiral TTFs, as a first step towards the elaboration of conducting and magnetic materials provided also with optical activity. In this respect, recent reports by Rikken et al. emphasized the influence of the chirality on the conducting properties of chiral single-walled carbon nanotubes, as a consequence of a new phenomenon called electrical magnetochiral anisotropy [13].

The recent availability of a series of chiral ethylenedithio-tetrathiafulvalenes containing monodentate oxazoline ligands (EDT-TTF-OX, **1a–c**) [11,14], in both racemic and enantiopure forms, prompted us to investigate their coordination properties towards the paramagnetic Cu(II) centre. We report herein the synthesis, single crystal X-ray structures and properties of these complexes. Moreover, the coordination of a potentially chelating bis(dentate) (*rac*)-TTF-thiomethyloxazoline **2** (EDT-TTF-(SMe)OX) [15] has been performed with both Cu(II) and Co(II) centres.

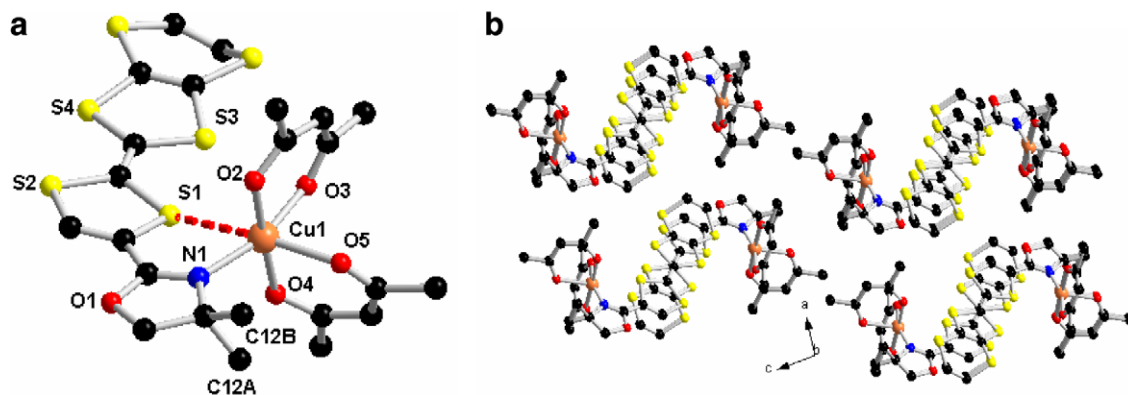
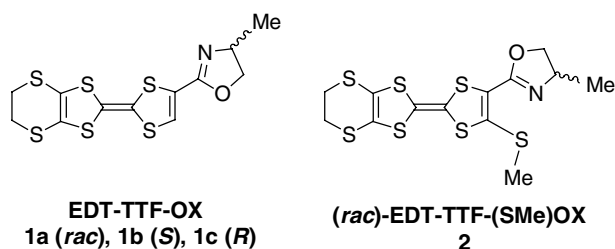


Fig. 1. (a) Crystalline structure of **3a**, with an emphasis on the coordination geometry around the Cu(II) centre. Fluorine and hydrogen atoms have been omitted for clarity. (b) Packing diagram for **3a**, showing the stacking of TTF along the *b*-direction.

2. Results and discussion

2.1. Synthesis and X-ray crystal structures of copper (II) complexes

The series of the paramagnetic complexes (EDT-TTF-OX)Cu^{II}(hfac)₂ (**3a–c**) has been conventionally prepared, by stirring a mixture of ligands **1a–c**, synthesized according to the published procedure [11], with the appropriate amount of [Cu(hfac)₂] precursor in a non-coordinating solvent, i.e. CH₂Cl₂–hexane mixture. This last feature is very important, since we observed that coordinating solvents remove the ligand out from the metal coordination sphere. Note that various [M(hfac)₂] precursors have been successfully used for the elaboration of molecular magnetic materials [16]. Suitable single crystals for X-ray analysis for the three compounds were grown upon slow evaporation of the solutions. The racemic complex **3a** crystallizes in the triclinic centrosymmetric space group *P* $\bar{1}$, with one independent molecule in the asymmetric unit cell in general position, whereas its enantiopure counterparts **3b** and **3c** crystallize in the triclinic chiral space group *P*1, although the cell parameters are identical. This implies that in **3b** and **3c**, there are two independent molecules in general positions. In the structure of complex **3a**, shown in Fig. 1a, one can observe a 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 at 2.192(4) Å (Table 1). The equatorial Cu···O and Cu···N distances range between 1.937(4) and 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).

It is well known that TTF sulfur atoms do not possess good coordination properties, therefore it is worth mentioning this interaction, all the more since metal···S_{TTF} short distances have been previously observed only in a

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