Coordination Chemistry Reviews 376 (2018) 277–291

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Molecular conductors of BEDT-TTF with tris(oxalato)metallate anions

Lee Martin

School of Science and Technology, Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, UK

ARTICLE INFO

Article history:
Received 30 May 2018
Received in revised form 13 August 2018
Accepted 13 August 2018

Keywords:
Tris(oxalato)metallate
BEDT-TTF
Superconductor
Metal
Semiconductor
Kosterlitz-Thouless

ABSTRACT

This review presents the synthesis, crystal structures and conducting properties of BEDT-TTF radical-cation salts with the tris(oxalato)metallate anion [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene]. This series has received much attention owing to the wide variety of conducting properties that have been observed. As well as including numerous metals, semiconductors and insulators, there are over twenty superconductors in this series. The series also includes several examples of multifunctionality where it has been possible to combine together particular physical properties in the same lattice such as electrical conductivity with magnetism, chirality or proton conductivity. This review presents an overview of the flexibility of the coordination chemistry of the oxalate ligand and the variety of packing arrangements of the tris(oxalato)metallate complexes in the insulating layers of these radical-cation salts.

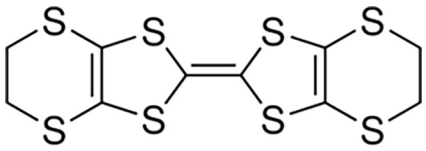
Contents

1. Introduction

Since the discovery of the first metallic charge-transfer salt of TTF-TCNQ in 1973 [1] extensive research has been performed in the field of molecular conductors with TTF derivatives. Studies of these 1-dimensional and 2-dimensional (1D and 2D) molecular conductors have investigated many interesting phenomena such as spin-Pieirls, charge order, Mott insulators, quantum spin-liquids, and spin density waves [2]. Organic superconductivity was first observed in a radical-cation salt of TMTSF (tetramethyltetraselenafulvalene) with the PF_6^- anion [3]. The majority of organic superconductors have been found with the donor molecule BEDT-TTF (Scheme 1), with κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ showing the highest Tc at ambient pressure, 11.6 K, whilst κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$ has a Tc of 13.1 K under applied pressure, and β′-$(BEDT\text{-}TTF)_2ICl_2$ has the highest Tc under applied pressure of 14.2 K [4]. Transition-metal complexes have been extensively used in radical-cation salts of BEDT-TTF because they offer the possibility of combining two or more properties in the same lattice. The most extensive family of these salts employs

E-mail address: lee.martin@ntu.ac.uk

https://doi.org/10.1016/j.ccr.2018.08.013
0010-8545/



Scheme 1. BEDT-TTF.

the tris(oxalato)metallate anion to combine conductivity with paramagnetism [5], ferromagnetism [6], or anti-ferromagnetism [7]. The ability of the tris(oxalato)metallate anion $[M(C_2O_4)_3]^{3-}$ to form infinite 2D sheets in a hexagonal network offers many possibilities for making subtle changes to the crystal structure, such as changing the metal centre, the counter cation, or the guest solvent molecule which is located within the hexagonal cavities of the 2D sheet. These small changes can have a drastic effect upon the crystal structure and thus the physical properties of the material. The bridging capability of the oxalato ligand has also made it possible to introduce two different metal centres into the same layer leading to long-range magnetic order. This review will focus on the molecular superconductors, metals, semiconductors and insulators derived from BEDT-TTF with tris(oxalato)metallate anions.

2. 4:1 radical cation-salts of BEDT-TTF with tris(oxalato) metallate(III)

Research into magnetic molecule-based materials that also exhibit conductivity by the group of Prof. Peter Day at the Royal Institution of Great Britain led to the discovery in 1995 of the first molecular paramagnetic superconductor in the radical-cation salt β″-(BEDT-TTF)$_4$[$(H_3O)Fe(C_2O_4)_3$]·PhCN (Fig. 1) [5,8–11]. This was an important discovery owing to the antagonistic relationship between superconductivity and magnetism. Several studies of the magnetic and electrical properties of this radical-cation salt observed the superconducting transition at 7.0–8.5 K, which is the highest Tc of all known BEDT-TTF/tris(oxalato)metallate superconductors to date.

2.1. Monoclinic β″ superconductors, metals and semiconductors

β″-(BEDT-TTF)$_4$[$(H_3O)Fe(C_2O_4)_3$]·benzonitrile crystallises in the monoclinic space group *C2/c* [5,8–11]. The asymmetric unit consists of two crystallographically independent BEDT-TTF$^{0.5+}$ molecules, half an $Fe(C_2O_4)_3^{3-}$ anion, half a solvent molecule, and half an H_3O^+ cation. The BEDT-TTF cations and tris(oxalato)ferrate anions are segregated into alternating layers (Fig. 1) with the donor molecules adopting a β″ packing arrangement (Fig. 2). The two crystallographically independent BEDT-TTF molecules pack in an AABBAABB sequence within each donor stack. Within each anion layer the tris(oxalato)metallate and the H_3O^+ cation adopt a hexagonal packing arrangement with the inner oxygens of the oxalato ligand octahedrally coordinated to the metal and the outer oxygens involved in hydrogen bonding with the H_3O^+ (Fig. 3). The

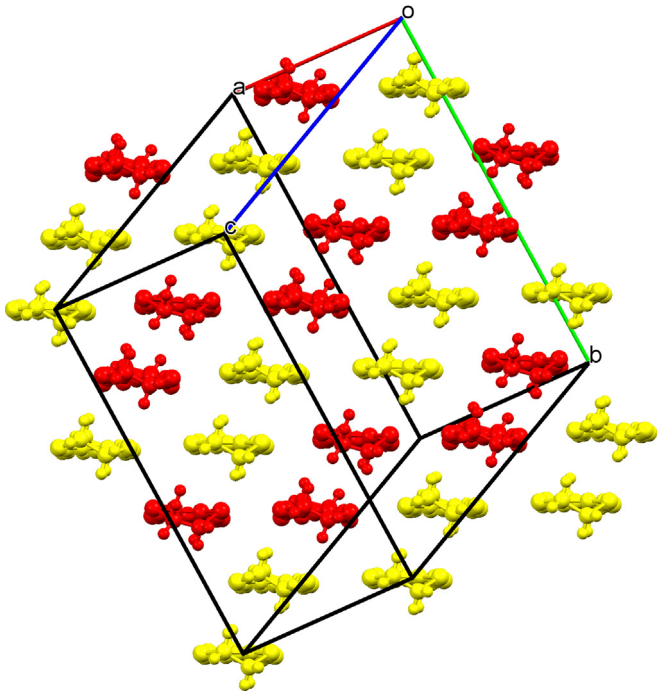


Fig. 2. BEDT-TTF donor layer in monoclinic β″ radical-cation salts. The two crystallographically independent BEDT-TTF molecules are coloured red (A) and yellow (B) and show the AABBAABB packing arrangement within a stack.

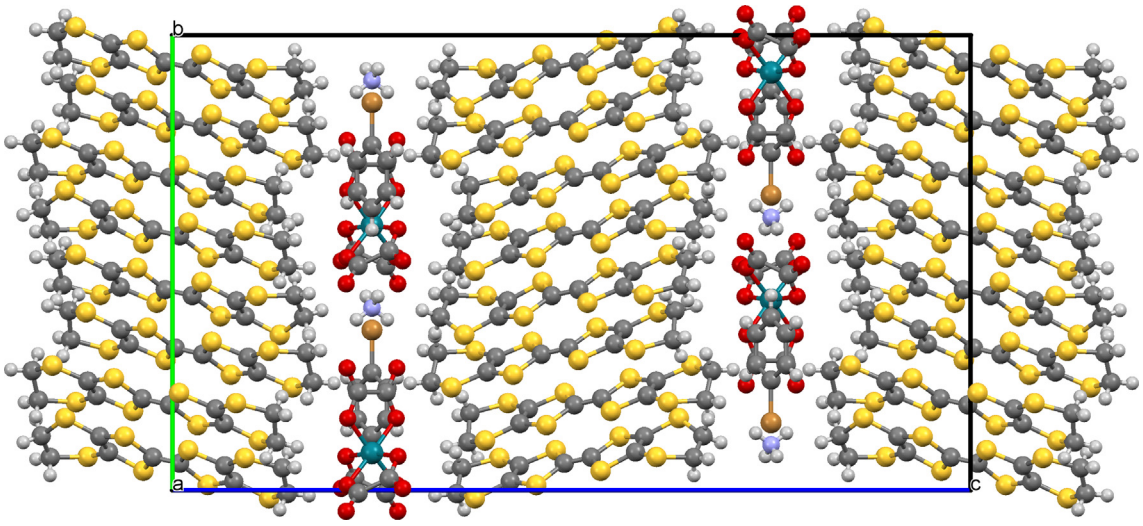


Fig. 1. Layered packing of monoclinic β″ radical-cation salts. Sulphur atoms are yellow, carbon grey, nitrogen blue, oxygen red and hydrogen white. The metal centre atoms are turquoise and halogen atoms are brown.