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A new organic metal with thedithiooxalato-bridged anion network, β″-ET)$_2${[NMe$_3$Ph]NaCr(C$_2$S$_2$O$_2$)$_3$(MeCN)}

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The synthesis, crystal structure, and conductivity of a new bis(ethylenedithio)tetrathiafulvalene (ET)-based cation radical salt with a β″-(ET)$_2${[NMe$_3$Ph]NaCr(C$_2$S$_2$O$_2$)$_3$(MeCN)} composition is described. The compound is metallic down to 60 K. In the structure, conducting donor layers with a β″-type packing alternate with $\{[\mathrm{NaCr(C_2S_2O_2)_3}]^{2-}\}_\infty$ anionic networks and $[\mathrm{NMe_3Ph}]^+$organic cation layers.

Key words: *organic conductors; cation radical salt; electrical conductivity; X-ray diffraction*

1. Introduction

The properties of organic conductors based on cation radical salts are essentially defined by the nature of the counter-ions. Small changes in their structure affect the properties of the resulting compounds. Recently, organic conductors of the $\mathrm{ET_4M^IM^{III}(C_2O_4)_3}$(solvent) family (ET – bis(ethylenedithio)tetrathiafulvalene) have been extensively studied [1–7]. Depending on the single charged cation $\mathrm{M^I}$, solvent, and trivalent metal $\mathrm{M^{III}}$, the compounds of this family exhibit phase transitions to a superconducting ($\mathrm{M^I}$ = H_3O, $\mathrm{M^{III}}$ = Fe, Cr, Ga) [1–5] or insulating state ($\mathrm{M^I}$ = H_3O, $\mathrm{M^{III}}$ = Fe, solvent – pyridine) [6], or reveal semiconducting ($\mathrm{M^I}$ = K, NH_4, $\mathrm{M^{III}}$ = Fe, Cr, Co, Al; solvent – PhCN) [4] or metallic behaviour ($\mathrm{M^I}$ = K, NH_4, $\mathrm{M^{III}}$ = Fe, Cr, solvent – DMF) [7] with decreasing temperature.

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In organic conductors of this family, M^{III}, M^{I}, and the solvent were varied while retaining a honeycomb structure of the anionic oxalato-based sheets. It is of interest to study the effect of substituting an oxalate ligand (ox) for a dithiooxalate one (dto) in the $[M^{III}(ox)_3]^{3-}$ anion on the stoichiometry, structure, and properties of the resulting ET compound. In this work, we report on the synthesis, crystal structure and conductivity of a new conducting ET-based cation radical salt containing a dithiooxalato-bridged honeycomb anion network with a β″-$(ET)_2[(NMe_3Ph)NaCr(dto)_3(MeCN)]$ composition.

2. Experimental

$[NMe_3Ph]_2NaCr(dto)_3$ was synthesized according to the procedure described in [8]. Single crystals of $(ET)_2\{[NMe_3Ph]NaCr(dto)_3(MeCN)\}$ (**1**) were obtained by the electrochemical oxidation of ET (7.6 mg, 2 mmol) at 16 °C in the presence of 30 mg of $[NMe_3Ph]_2NaCr(dto)_3$ under an argon atmosphere and at a current of 0.1 μA. Thick shiny plates were collected after two weeks.

The resistivity of single crystals was measured down to 4 K by a standard dc four -probe technique with graphite paste.

The main crystallographic data for β″-$(ET)_2[(PhMe_3N)NaCr(dto)_3(MeCN)]$ are: $C_{37}H_{33}CrN_2NaO_6S_{22}$, the triclinic centro-symmetrical space group, $P\bar{1}$, $a = 10.335(2)$, $b = 11.211(2)$, $c = 26.016(5)$ Å, $\alpha = 82.79°$, $\beta = 86.63°$, $\gamma = 62.64°$, $V = 2656(1)$ Å^3, $d_{calcd} = 1.728$ g/cm^3, and $Z = 2$. The structure was solved by direct methods using the SHELXL-97 program suite [9]. The final refinement parameters were $R = 0.0957$, and GOOF = 0.964.

3. Results and discussion

The compound **1** was precipitated by the electrochemical oxidation of ET from a constant-current electrocrystallisation cell using a low concentration solution of $[NMe_3Ph]_2NaCr(dto)_3$ in MeCN. The crystals of **1** form shiny and thick elongated plates. The compound loses the solvent during storage, the crystal surface losing its lustre and becoming rough.

1 has a layered structure. The crystal structure is characterized by four alternating layers along the *c* direction in the sequence: ET, $[NaCr(dto)_{3]}\}_\infty$, $[NMe_3Ph]^+$ cations together with CH_3CN molecules, and $[NaCr(dto)_3]_\infty$. The ET molecules are aligned side-by-side and form a 2D array within the *ab* plane shown in Fig. 1, in which a view of the ET cation layer along the longer axis of the donor molecule is presented. Numerous shortened S…S intermolecular contacts exist between molecules within the donor cation layer, giving the material a two-dimensional electronic character. The overall donor ion packing exhibits the so-called β'' type [10] donor arrangement, which often occurs in conducting ET salts.

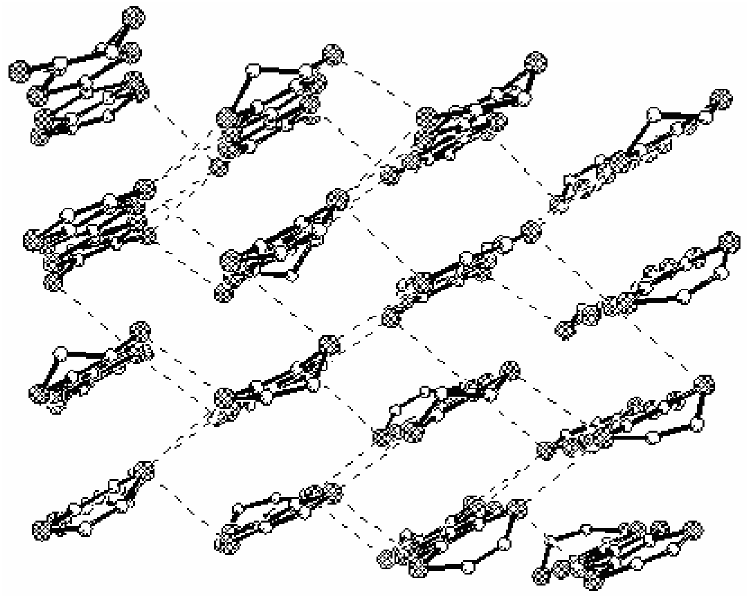

Fig. 1. View of the ET cation layer along the longer molecular axis

Each $[NaCr(dto)_3]_\infty$ sheet has a honeycomb arrangement, in which Na and Cr alternate to form an approximately hexagonal network. Organic $[NMe_3Ph]^+$ cations are enclosed between the two $[NaCr(dto)_3]_\infty$ sheets. Half of the cations are intercalated in the first network and the other half are intercalated in the other.

No short interatomic S…S contacts were found between the ET donor layers and anionic ones. The shortest distance from the S dto atom to the S atom of ET (S1…S13) was 3.74 Å. This value exceeds that of a normal van der Waals S…S contact, namely 3.60 Å [11].

Of the ET cation-radical salts usually comprising a donor and one anion, the salt **1** has both an unusual composition and structure. Apart from the donor, it contains the $[Cr(dto)_3]^{3-}$ anion, two different cations and a solvent molecule, and can be said to be a four(multi)-component system, similarly to the so-called three-component $ET_nM^IHg(SCN)_4$ family [12, 13]. In the three-component $ET_nM^IHg(SCN)_4$ system, as well as in β''-$ET_4[M^IM^{III}(ox)_3]\cdot$(solvent), there is a third component M (alkali metal, ammonium, or hydroxonium cations) which participates during the formation of the polymeric network of an insulating layer. In contrast to the above-mentioned families, whose structures involve only two alternating layers (ET and a polymeric network), the polymeric anion networks in the title compound alternate with either ET or $[NMe_3Ph]^+$ layers. In fact, the packing motifs of two structures are combined in one structure: β''-$ET_4[M^IM^{III}(ox)_3]\cdot$(solvent) [1–7] and the molecular ferromagnet $[Bu_4N]$

[MnCr(ox)$_3$] [14]. The most important difference between the crystal structures of **1** and the molecular ferromagnet [Bu$_4$N][MnCr(ox)$_3$] is that the number of [NMe$_3$Ph]$^+$ cations in the cation layer of **1** is twice as large as the number of [Bu$_4$N]$^+$ cations in [Bu$_4$N][MnCr(ox)$_3$] Also, in **1** they are intercalated in both of the nearest networks, while the organic cations in [Bu$_4$N][MnCr(ox)$_3$] are intercalated only in one network [14].

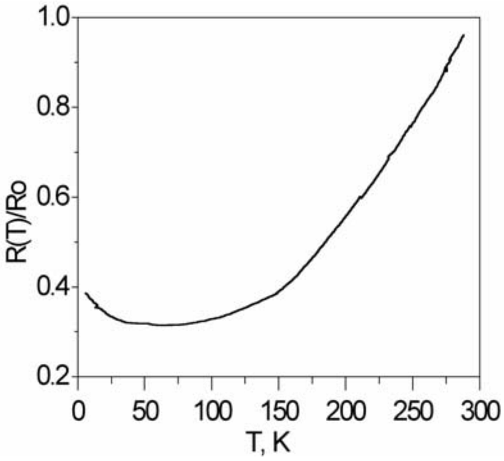

Fig. 2. Temperature dependence of relative electrical resistance for a single crystal of β″-(ET)$_2${[NMe$_3$Ph]NaCr(dto)$_3$(MeCN)}

Conductivity data for **1** are shown in Fig. 2. (ET)$_2${[NMe$_3$Ph]NaCr(dto)$_3$(MeCN)} is metallic at room temperature, with σ_{298K} = 120 S·cm^{-1}. With decreasing temperature, the complex remains metallic down to 60 K. At lower temperatures, its resistance smoothly rises, being lower than the room-temperature value. In this case, a gradual localization of conduction electrons appears to be caused by the quality of the crystal and impurities.

4. Conclusion

A new metallic ET cation radical salt with a dithiooxalato-bridged honeycomb anion network, namely (ET)$_2${[NMe$_3$Ph]NaCr(C$_2$S$_2$O$_2$)$_3$(MeCN)}, has been synthesized and characterized. The conducting layers in this cation radical salt alternate with three insulating layers and adopt the β″-packing motif found in other ET cation radical salts. In fact, the crystal structure of this compound combines the features characteristic of both β″-ET-oxalatometallates and the molecular ferromagnet [Bu$_4$N][MnCr(ox)$_3$]. The title compound is metallic with the room temperature conductivity of 120 S·cm^{-1}. Below 60 K, its resistance smoothly increases on decreasing temperature, not attaining, however, the room-temperature value.

Acknowledgements

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