device with an identical layer structure was fabricated using commercial ITO on glass (Colorado Concept Coating, LLC, cleaned in an oxygen plasma). The 0.2 × 0.5 cm^2 OLED emitting areas were defined by shadow masks. Light output and *J–V* characteristics were measured with a Keithley 2400 source meter and IL 1700 radiometer at 25 °C.

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Metallic Conductivity in a Polyoxovanadate Radical Salt of Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF): Synthesis, Structure, and Physical Characterization of β''-(BEDT-TTF)$_5$[$H_3V_{10}O_{28}$]$\cdot$4H_2O**

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Polyoxometalate compounds are having a large impact in many different disciplines of current interest, such as catalysis, medicine, materials science, and magnetism, due to their rich and tunable molecular and electronic properties.[1,2] The role of polyoxometalates has been of special relevance in the field of functional molecular materials. The structural and chemical stability of these compounds has made them perfect electroactive components for the construction of materials formed by two molecular networks with the aim to combine two distinct physical properties in the same material. In this context, one of the most appealing and still challenging combinations is that of electrical conductivity, and even superconductivity, with magnetism.[3] These hybrid materials are usually prepared as crystalline salts formed by organic electron donor molecules (tetrathiafulvalene (TTF) derivatives), responsible for the electrical conductivity, and by inorganic anions responsible for the magnetic properties. Many radical salts of polyoxometalates have been reported so far.[4] Often they show novel organic packings and can exhibit coexistence of conducting electrons and localized magnetic moments. The finding of metallic states in this type of salts, however, is difficult because the large charges of the polyanions usually induce charge localization on the organic sublattice. In fact, most of the polyoxometalate salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) are semi-conductors, or have phase transitions to a semiconducting state at high temperatures. Only three radical salts are known to present "light" metallic regimes that disappear below 200 K.[5]

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It is important to notice that all the above radical salts are based on polyoxomolybdates and polyoxotungstates. To the best of our knowledge no radical salts of polyoxovanadates have been reported, although the vanadium-containing polyanions present a wide range of interesting properties associated with their distinctive topologies and electronic structures.[6] These anions can show compact structures like $[V_{10}O_{28}]^{6-}$,[7] open complexes with ribbon, basket, or shell shapes,[8] or even close host structures that can uptake neutral or ionic guests.[9] Many giant clusters are also known, for example, the $\{V_{19}\}$ cluster family.[10] Another feature of polyoxovanadates are their remarkable redox processes that make them interesting in bioinorganic chemistry,[11] magnetochemistry,[12] sensor technology,[13] and catalysis.[14] Moreover, they are potential candidates for anodes in lithium-ion batteries.[15]

The introduction of polyoxovanadates in the field of the radical salts can expand the range of molecular materials based on polyoxometalates. As they present different sizes, shapes, and charges to those of the commonly used polyoxomolybdates and polyoxotungstates, new interactions and packings in the organic layers can be induced that could affect, and even improve, the conducting properties of the materials. In this work, we present the first radical salt formed by the combination of the BEDT-TTF molecule with the polyoxovanadate $[H_3V_{10}O_{28}]^{3-}$ (see Fig. 1).

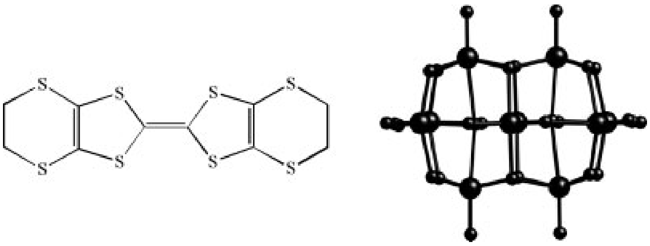

Figure 1. The donor BEDT-TTF (left) and the polyoxovanadate $[H_3V_{10}O_{28}]^{3-}$ (right).

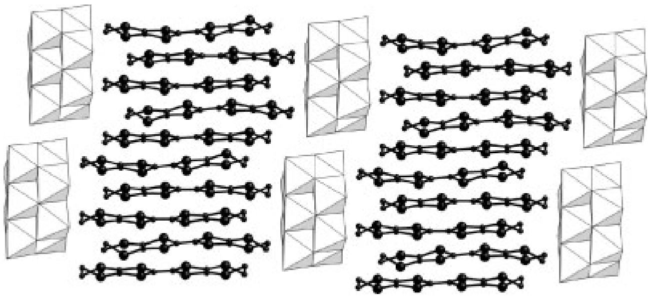

Figure 2. Packing diagram of BEDT-TTF$_5$[$H_3V_{10}O_{28}$]. View on the *AC* plane showing the alternating organic–inorganic layers present in the structure.

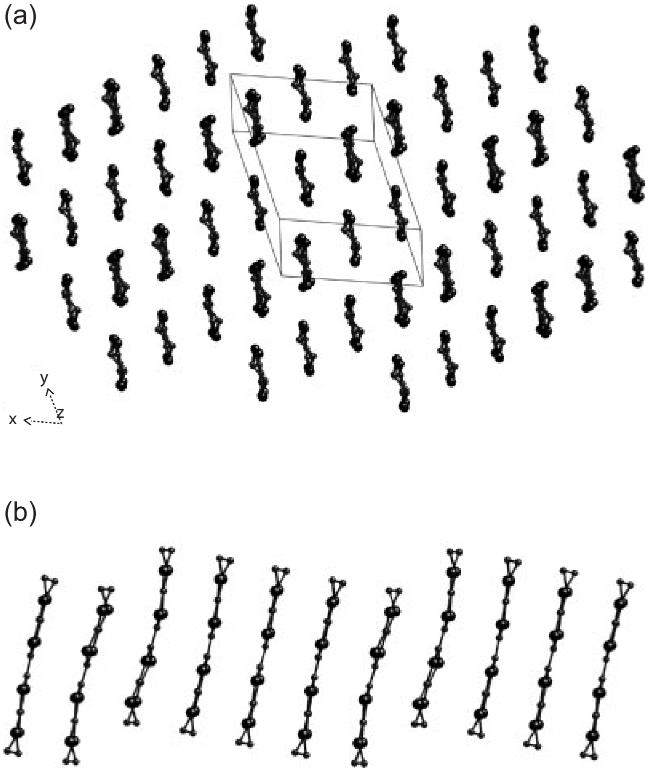

Figure 3. a) Side view of the organic layer, showing the β″-phase disposition of the BEDT-TTF molecules; b) stacking mode in the chain of the BEDT-TTF molecules along the *a*-axis.

The title compound was obtained by electrochemical oxidation of BEDT-TTF in a dichloromethane/dimethylformamide mixture in the presence of $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$. Shiny black crystals were obtained on the anode side after several days. The structure of this compound is formed by alternating layers of polyoxovanadate anions and layers of BEDT-TTF molecules (Fig. 2). Three crystallographically independent BEDT-TTF molecules, A, B, and C, were found with A located at a centre of symmetry. The layer adopts a packing motif typical of the so-called β″-phases (Fig. 3).[16] It is composed of stepwise parallel chains of BEDT-TTFs that run along the *a*-axis formed by the repetition of groups of five eclipsed BEDT-TTFs, following the sequence ...CBABC... The chains are displaced to one another with interchain distances being shorter than the intrachain ones. The shortest S···S interchain contacts range from 3.32 to 3.55 Å, whereas the intrachain ones range from 3.75 to 3.84 Å. The interchain distances are much shorter than the sum of the van der Waals radii (3.6 Å), showing that the system is really two-dimensional and that the overlap of the organic radicals is important. Both characteristics are key features for the electrical properties of this material.

The polyoxovanadate layer adopts a pseudo-tetragonal arrangement. Each anion has three protonated oxygen atoms that are engaged in hydrogen bonding as denoted by the short distances observed between the anions (O12t–O11t = 2.73 Å).

Another important feature is the presence of several strong intermolecular contacts between the organic and the inorganic layers. Two kinds of interactions can be observed: 1) between the sulphur atoms of the BEDT-TTF molecules and some oxygen atoms of the polyoxoanions, with the shortest S···O distances ranging from 2.93 (S7–O4) to 3.26 Å (S18–

O3); and 2) between several O atoms of the anions and hydrogen atoms from the ethylene groups (shortest C···O distances ranging from 3.02 (C17–O17) to 3.15 (C9–O14t) Å, too long to be considered hydrogen bonds). The 5:1 stoichiometry suggests a mixed valence state in the organic part, with three positive charges distributed over the five BEDT-TTFs. One can roughly estimate the degree of ionicity of each BEDT-TTF from the bond distances of the fulvalene ring.[17] This method suggests that A-type molecules are completely ionized, while C-type and B-type have a charge close to +0.5. The overall charge on the organic molecules is in agreement with the trianionic charge, and the presence of partially oxidized BEDT-TTF molecules in an extended bidimensional network of interactions is expected to favor electrical conductivity.

Magnetic susceptibility (χ_m) measurements were performed on polycrystalline samples with a superconducting quantum interference device (SQUID) magnetometer in the temperature range 2–300 K and with an external magnetic field of 1000 G (1 G = 10^{-4} T). The $\chi_m T$ product shows a linear dependence versus temperature (T), decreasing monotonically from its value at room temperature (1.15 emu K mol^{-1}) down to 0.035 emu K mol^{-1} at 2 K. This behavior is characteristic of a weak temperature-independent paramagnetism, consistent with a delocalization regime of the electrons in the extended organic network (Pauli-type paramagnetism). In addition to this predominant contribution, a small Curie tail is also observed in χ_m at very low temperatures, as usually found in this kind of compounds and ascribed to the unavoidable presence of structural defects. The data can be fitted taking into account these two contributions:

$$\chi_m = C/T + \chi_{TIP} \qquad (1)$$

where $\chi_{TIP} = 4.0 \times 10^{-3}$ emu mol^{-1}, and $C = 0.014$ emu K mol^{-1}. The value obtained for χ_{TIP} is typical for other TTF-based conductors, while C is very small, indicating that the presence of structural defects in this case is quite marginal. No contribution from the anions, which are diamagnetic, was observed.

Four probe electrical resistivity (ρ) measurements on single crystals show a metallic behavior (Fig. 4). The electrical conductivity, $\sigma = 1/\rho$, increases from 235 S cm^{-1} at room temperature up to 350 S cm^{-1} at 135 K, followed by a gradual decrease upon further cooling. The analysis of the derivative d$\ln\rho$/d($1/T$) (Fig. 4b) shows a sharp maximum at approx. 48 K, indicating the appearance of a semiconducting regime at this temperature. This feature should be associated with the opening of a gap and not with gradual charge localization. Thermoelectric power measurements were also performed on single crystals by attaching the sample with two gold wires to two quartz blocks that were alternatively heated with gradients of 1 K. The Seebeck coefficient value at room temperature is

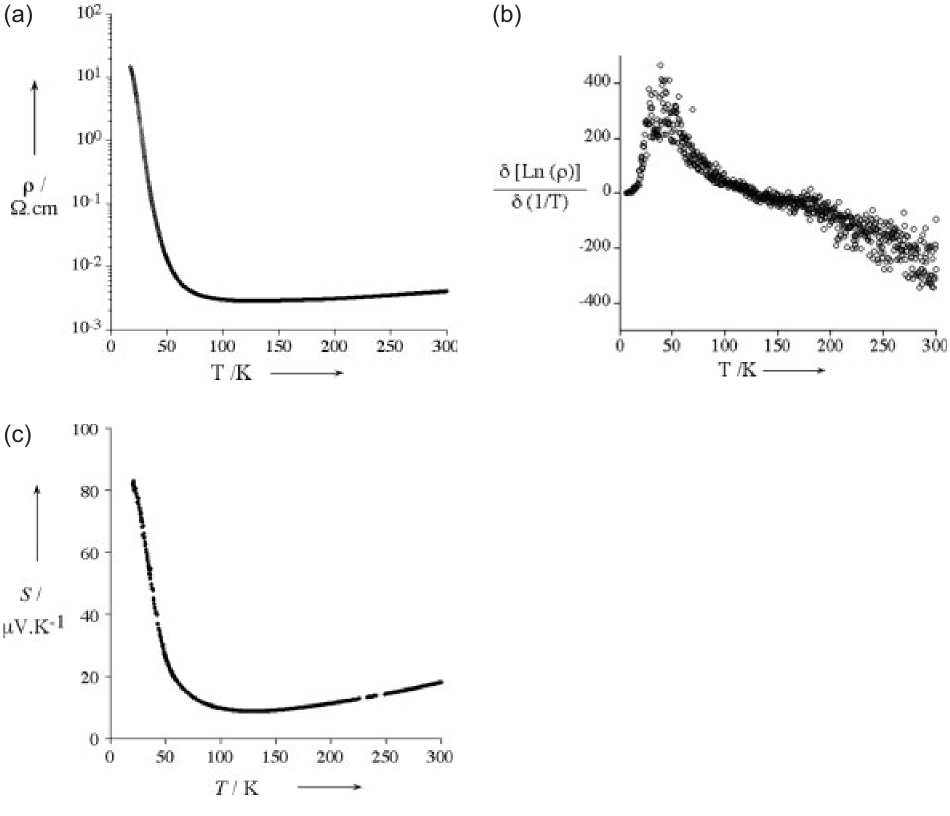

Figure 4. Electrical transport properties of BEDT-TTF$_5$[H$_3$V$_{10}$O$_{28}$]: a) Temperature dependence of the electrical resistivity, ρ; the derivative d$\ln\rho$/d($1/T$) is shown in (b). c) Temperature dependence of the Seebeck coefficient.

$S = 18$ μV K^{-1}. This is a small value, typical of molecular metals. Furthermore, the metallic regime at high temperatures is confirmed by the decrease of the thermopower, almost proportional to T, down to ~124 K where it reaches a minimum value of 8.74 μV K^{-1}, followed by a gradual increase upon further cooling. However, in agreement with conductivity data, a typical semiconducting behavior with $S \propto (1/T)$ is only observed below 50 K. (Fig. 4c).

From these electrical transport measurements two main conclusions can be drawn. First, the high-temperature behavior is typical of a molecular metal, in good agreement with the magnetic measurements. And second, the low temperature semiconducting regime is associated with the opening of an energy gap around 50 K, proceeded by a fluctuating regime with a gradual onset upon cooling below ~140 K.

In conclusion, the first radical salt of BEDT-TTF with a polyoxovanadate has been prepared and characterized as a metal. This is also the first example of a radical salt formed by the BEDT-TTF organic donor and a polyoxometalate with a wide range of metallic conductivity; the high conductivity observed at room temperature being also noteworthy. This work opens the way for new radical salts based on polyoxovanadates, with special interest in salts analogous to the title compound obtained by varying the oxidation state of the polyoxovanadate, which can be reduced by several electrons. If the structural features can be maintained, this would allow us to vary the population of the conduction band of the organic layer and therefore to tune the conducting properties. Also, in such a system, it would be of interest to study the interaction between delocalized electrons in the organic sublattice and the localized moments in the paramagnetic mixed valence polyoxovanadate, which in the present case are due to delocalized electrons hopping among all the metal centers of each cluster.

Experimental

Black single crystals of (BEDT-TTF)$_5$[H$_3$V$_{10}$O$_{28}$]·4H$_2$O were obtained by the electrochemical oxidation of bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF, 2.6×10^{-3} M) in the presence of [(n-C$_4$H$_9$)$_4$N]$_3$[H$_3$V$_{10}$O$_{28}$] (3×10^{-3} M) in a U-shaped cell with Pt electrodes (1 mm of diameter) separated by a sintered-glass frit. The crystallization took place after 6 days when using dichloromethane and dimethylformamide as solvents (7:3) and a low constant current of 0.6 μA. The solvents were not previously dried, and it was necessary to add some drops of water to obtain good quality single crystals.

X-ray Crystallography: $C_{50}H_{51}O_{32}S_{40}V_{10}$, $M_w = 2955.70$, triclinic, space group $P1$, $a = 10.747(5)$, $b = 11.490(5)$, $c = 20.62(2)$ Å, $\alpha = 77.80(4)$, $\beta = 78.48(4)$, $\gamma = 67.35(3)°$, $V = 2277(3)$ Å^3, $T = 110(2)$ K, $Z = 2$, $D_c = 2.156$ mg m^{-3}, graphite monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å), Bruker charge-coupled device (CCD) diffractometer, $F(000) = 1477$, $\mu = 1.973$ mm^{-1}, 0.35 mm × 0.26 mm × 0.03 mm, 10 519 reflections measured, 6500 unique ($R_{\text{int}} = 0.0815$). The structure was solved by direct methods followed by Fourier synthesis, and refined on F^2 (SHELX-97: G.M: Sheldrick, University of Göttingen, 1997). The non-hydrogen atoms were refined anisotropically, except for the disordered ones. The final refinement led to $R(F) = 0.075$ and $R_\omega(F2) = 0.1844$ for 2522 reflections [$I > 2\sigma(I)$]. H-atoms were placed in the calculated positions. Cambridge Crystallographic Data Centre (CCDC) 199 959 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; E-mail: deposit@ccdc.cam.ac.uk].

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