

Mixed-valence Bis(ethylenedithio)tetrathiafulvalenium (BEDT-TTF) Monolayers Sandwiched Between Extended Close-packed Keggin-type Molecular Metal Oxide Cluster Arrays: Synthesis, Unprecedented Acentric Structure, and Preliminary Conducting and E.S.R. Properties of (BEDT-TTF)₈SiW₁₂O₄₀

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The synthesis, acentric sandwich structure, and preliminary electronic properties of conducting plate-like single-crystals of a 3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalene (BEDT-TTF) salt of the tetravalent 12-tungstosilicate molecular anion SiW₁₂O₄₀⁴⁻ are described as well as evidence for a correlation between the non-centrosymmetrical character of the bi-dimensional solid and that of the discrete molecular cluster anion.

Size, shape, multi-stage redox states,¹ and an acentric molecular configuration are some of the remarkable molecular features of heteropolyions with the α -Keggin structure, exemplified by SiW₁₂O₄₀⁴⁻,² which make them attractive precursors for the preparation of charge-transfer hybrid salts of organic-inorganic character. Of particular interest is the expectation of novel architectures and electronic properties of such hybrids, as was the case when large, all-inorganic, redox-active, albeit centrosymmetrical molecular halide³⁻⁵ and chalcogenide^{6,7} cluster anions and, recently, organometallic acceptors,⁸ were associated with tetrathiafulvalene and several of its substituted derivatives. In this Communication we report the preparation, unique two-dimensional acentric structure, and preliminary characterization of the title compound, the first example of a novel class of conducting organic donor-polyoxometallate extended sandwich. In addition, we point out that the acentricity of the molecular anion extends to the unusual inorganic layer resulting in different orientations of the arrangement of oxygen atoms at its top and bottom. We further note that the acentric character of the compound seems to arise from specific adaptations of the ethylene end-groups of the organic donor molecules to the different sides of the acentric inorganic network, thereby exemplifying a direct correlation between the non-centrosymmetrical character of a molecular building block and that of the solid. This possibly represents a new concept in the design of a novel non-centrosymmetrical solid. Note also that the nature and properties of this new class of salts add to the recent increased interest in the solid-state chemistry of these soluble metal oxide analogues.⁹

Black, shiny plate-like single-crystals of the title compound were grown at a platinum wire anode by constant current electrolysis (1.8 $\mu\text{A cm}^{-2}$) at $30 \pm 0.2^\circ\text{C}$ of an acetonitrile/1,1,2-trichloroethane (4/1) mixture containing the organic donor¹⁰ ($2 \times 10^{-3}\text{ M}$) and the tetraethylammonium salt¹¹ of the 12-tungstosilicate ion, [Et₄N]₄SiW₁₂O₄₀ ($4 \times 10^{-3}\text{ M}$). The stoichiometry was determined by resolution of the crystal structure.[†]

The crystal structure (Figure 1) consists of two-dimensional organic and inorganic sub-lattices alternating along the unique axis [010] of the monoclinic unit cell, an arrangement which so far has only recently been described for the quasi-two-dimensional salts with polymeric anion layers (BEDT-TTF)₃Ag₄I₈^{12,13b} and (BEDT-TTF)₂Cu₅I₆.¹⁴ Therefore, the ability of the large, essentially spherical polyoxometallate anions to form single pseudo-close-packed hexagonal layers (Figure 2) is demonstrated here. The BEDT-TTF radical-cations act as interstitial species at specific sites (Figure 2) of these two-dimensional molecular metal oxide cluster arrays, yet they are not merely interspersed or intercalated in the solid. Rather, the organic molecules are arranged into two types of stacks which are anchored differently to the anion network. Thus, both ethylene groups of the molecules of the stacks labelled (I) in Figure 2 fit essentially the same type of interstices in between the anions (Figure 1) and therefore the

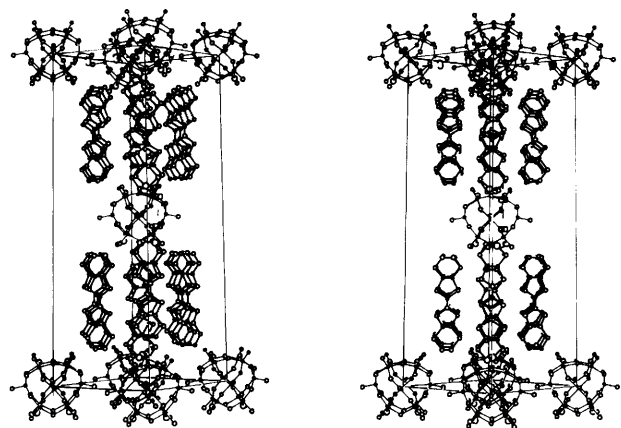


Figure 1. Stereoscopic view of the unit cell along the stack $a + c$ diagonal direction (ORTEP). The central SiO₄ tetrahedron of each polyoxotungstate has been omitted in the drawing.

[†] Crystal data for C₈₀H₆₄O₄₀S₆₄SiW₁₂, $M = 5971.76$, monoclinic, space group $I2$, $a = 14.017(3)$, $b = 43.259(6)$, $c = 14.065(5)$ Å, $\beta = 107.26(2)^\circ$, $V = 8144.5$ Å³, $D_c = 2.42$ g cm⁻³, $Z = 2$. The well developed face of the single crystals correspond to (010). X-Ray diffraction data were collected on a Enraf-Nonius CAD4-SDP diffractometer system using the ω - 2θ scan technique with graphite-monochromated Mo- K_α radiation. A total of 6964 independent reflections were measured (to $2\theta = 50^\circ$), of which 5204 were judged to be 'observed' [$I \geq 3\sigma(I)$]. The data were corrected for absorption ($\mu = 94.8$ cm⁻¹) by a semi-empirical method based on ψ -scans. The structure was solved by a combination of Patterson and direct methods and least-squares refinements reached $R = 0.054$ ($R_w = 0.079$) with a goodness-of-fit value of 1.617. Because of the limited number of reflections available from the room-temperature data collection and the considerable number of parameters to be determined, only the six tungsten atoms were refined anisotropically; the remaining atoms (32 S, 20 O, 42 C, and one Si) of the asymmetric unit were refined isotropically to convergence. The thermal parameters for the oxygen atoms are normal (isotropic B values 2.2–4.8) except for the bridging oxygen atom O(56) (8.2 Å²). Also the B values for two ethylene carbon atoms of different molecules, namely C(20) and C(59) are 10.2 and 9.1 respectively, indicating disorder as commonly observed for BEDT-TTF salts.^{13a} Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

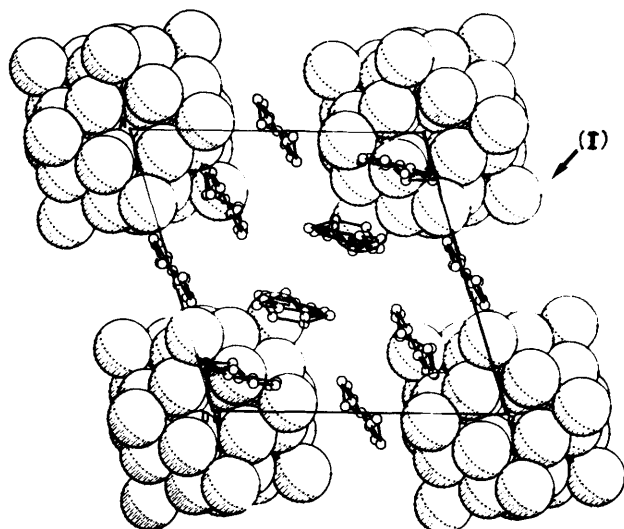


Figure 2. Projection of one organic layer (ORTEP, ball-and-stick) on the (a, c) plane emphasizing its interstack mode of packing and its anchoring on the $\text{SiW}_{12}\text{O}_{40}^{4-}$ (PLUTO, space-filling) layer.

donor molecules in (I) stack uniformly on top of each other. In particular, there is no relative displacement along the long molecular axis between two neighbouring donors in stack (I) (Figure 1) and only a uniform small displacement along their short molecular axis (Figure 2). The type (II) stacks (unlabelled in the Figure for clarity) are neatly interwoven with the molecular oxide clusters in such a way that each of the ethylene groups of any molecule has a different environment since it faces either an anion or a hole along [101] (Figure 1). In addition, the sequence along this direction is such that pairs of molecules are required to match alternately the anions and the holes. In other words, the type (II) stacks result from a zig-zag mode of stacking of BEDT-TTF dimers. The intradimer overlap is similar to that between successive molecules in stacks (I). As exemplified in Figure 2, a W-mode type of packing^{13c} is observed along the interstack direction. The molecules are loosely packed along the stacks since the shortest intermolecular $\text{S} \cdots \text{S}$ distances are 3.88 and 4.04 Å; and 3.78, 3.84 and 3.89 Å for the stacks (I) and (II) respectively. The $\text{S} \cdots \text{S}$ interactions appear to be stronger along the interstack direction since the shortest distances are of the order of the van der Waals separation (3.60 Å) with one short contact at 3.38 Å. The $\text{SiW}_{12}\text{O}_{40}^{4-}$ anion is located on the 2-fold axis and has the classical α -Keggin structure.² The sets of W-O bond lengths corresponding to the three types of

oxygen atoms [central tetrahedron O_a , 2.34(1)–2.41(1) Å; bridging $\text{O}_{b,c}$, 1.79(3)–1.98(4) Å; and terminal O_d , 1.65(2)–1.74(2) Å] are in the expected ranges.¹⁵

The electrical conductivity is activated [$\sigma(300\text{ K})$ 2.0 $\Omega^{-1}\text{ cm}^{-1}$, $E_a = 0.29\text{ eV}$]. Consistently, preliminary room-temperature e.s.r. measurements reveal the presence of a single line with anisotropic characteristics [g 2.011 along the thin direction of the crystals (b axis); 2.005 in the (a, c) plane; and $\Delta H = 45$; 30 G respectively (1 G = 10^{-4} T)] typical of localized BEDT-TTF spins.⁷

Finally, the oxygen atom arrangements at the top (Figure 2) and bottom faces of any inorganic layer are rotated by 90° since (i) the α -Keggin structure² presents an average T_d symmetry; (ii) the translational symmetry-related in-plane anions have the same orientation. Therefore, the inorganic anion layer itself is non-centrosymmetrical. The mode of alternated stacking of the organic and inorganic layers on top of each other is such that this acentric character is transferred in the transverse b direction to the whole solid *via* specific C–H \cdots O hydrogen contacts.

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