



Hybrid Material Based on the Lindquist Polyoxometalate $[W_6O_{19}]^{2-}$ and the organosulfur donor o-Me₂TTF: A Combined Structural and Spectroscopic Study

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ORIGINAL PAPER

Hybrid Material Based on the Lindquist Polyoxometalate
[W6O19]22
and the organosulfur donor o-Me2TTF: A Combined
Structural and Spectroscopic Study

Eric W. Reinheimer •
Damian Jankowski •
,

Roman S wietlik •
Marc Fourmigue´

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Abstract The synthesis, crystal structure and spectroscopic
properties of the hybrid radical cation salt containing oxidized
o-3,4-dimethyltetrafulvalene (o-Me2TTF) and the Lindquist
polyoxometalate anion [W6O19]2- are reported. The
title salt represents the first time a Lindquist polyoxometalate
has been utilized as the counter anion with this unsymmetrical
member of the TTF family of derivatives. The salt crystallizes
in the triclinic space group P1 with $a = 7.6211(7) \text{ \AA}$,
 $b = 9.5231(9) \text{ \AA}$, $c = 12.2148(11) \text{ \AA}$, $\alpha = 105.5870(10)^\circ$,
 $\beta = 106.8340(10)^\circ$, and $\gamma = 95.6950(10)^\circ$. Resolution of the
solid state structure revealed that the o-Me2TTF radical cations
aggregate as isolated face-to-face dimers with intradimer
interactions between neighboring sulfur atoms at distances
 $\sim 3.6 \text{ \AA}$. Hydrogen bonding was also observed between
hydrogen atoms bound to sp2-hybridized carbon atoms of
o-Me2TTF and bridging oxygen atoms of [W6O19]2-. Single
crystal IR and Raman spectra were also collected and provide
further evidence that the o-Me2TTF donors have been oxidized
to their corresponding radical cationic states.

E. W. Reinheimer •
M. Fourmigue´
Institut des Sciences Chimiques de Rennes, UMR 6226
CNRS-Universite´ Rennes 1, Campus de Beaulieu,
35042 Rennes, France
,

Institute of Molecular Physics, Polish Academy of Sciences,
ul. M. Smoluchowskiego 17, 60-179 Poznań, Poland

D. Jankowski •
R. S wietlik
Present Address:

E. W. Reinheimer (&)
Department of Chemistry and Biochemistry and W.M. Keck

Foundation Center for Molecular Structure, California State
University San Marcos, 333 S. Twin Oaks Valley Road,
San Marcos, CA 92096, USA
e-mail: ereinhei@csusm.edu
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Introduction

A focus of contemporary Materials Science is the preparation of molecule based materials that display active physical properties such as conductivity, ferromagnetism or non-linear optical properties [1]. With the initial discovery of metallic conductivity in TTF-TCNQ as well as the first and second generation of organic superconductors, materials containing oxidized organosulfur (or organoselenium) donors were identified as those most likely to display elevated conductivity (or superconductivity) [2-4]. Most advantageous to the observation of either non-activated conductivity or superconductivity within these materials was the solid state aggregation of the oxidized donors into long range stacks which created a more facile pathway for the transfer of itinerant electron density.

As the study into electroactive materials persisted, interest in materials that displayed multifunctionality began to manifest. Through the directed, rational synthesis of solid networks in the form of salts, where each ionic network furnished a distinct physical property to the material, the multifunctional materials known as magnetic conductors were prepared [5]. The molecular ferromagnet, (BEDT-TTF)₃[MnCr(C₂O₄)₃].CH₂Cl₂ (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene or ET) served as a 'proof of concept' because conducting layers of partially oxidized ET donors were successfully combined with paramagnetic layers of oxalato-bridged bimetallic complexes to form a material which displayed both metallic conductivity ($\rho_{RT} = 250 \text{ S cm}^{-1}$) and ferromagnetically coupled metal atoms ($T_c = 5.5 \text{ K}$) [6].

Oxalato-bridged bimetallic anions are not the only class of inorganic anions studied in the preparation of hybrid

salts containing derivatives of TTF. In an effort to further study how novel lattice architectures and physical properties resulting from the association of organic radical cations can be affected by large anions, the use of large polyoxometalate clusters as anions in hybrid salts has been probed. Due to their elevated solubility in organic solvents, ability to possess variable charges and shapes which may alter the corresponding band structure and possibility of incorporating paramagnetic metal atoms into the polyoxoanion core, this class of anions is an ideal candidate for incorporation into hybrid and multifunctional materials [7].

With the Lindquist clusters, with the formula $(M_6O_{19})^{2-}$ ($M = Mo$ or W), 2:1 phases involving TTF, TMTTF (tetramethylnitratetetrathiafulvalene), ET, BET-TTF (bis(ethylenedithio)tetrathiafulvalene), TPTTF (tetraphenyltetrathiafulvalene) and DMDPTTF (dimethyldiphenyltetrathiafulvalene) have been reported [8–13]. Later a 2:1 phase involving $[W_6O_{19}]^{2-}$ and the donor bis(propylene)dithiotetrathiafulvalene (BPDTTTF) was communicated [14]. In all cases, those salts were found to contain isolated dimers of radical cations and were insulating. Meanwhile, 3:1 and 4:1 phases containing TTF and TMTSF were discovered and found to be semiconducting [15, 16]. Finally, a 5:1 hybrid salt involving ET and the substituted Lindquist anion $[V_5W_{10}O_{43}]^{3-}$ which displayed metallic conductivity, was reported by Ouahab and coworkers in 1993 [17]. While the Lindquist polyoxometalates have yielded a large number of results, other polyoxoanion clusters have also yielded salts when combined with TTF derivatives such as ET. When ET was combined with the polyoxovanadate cluster $[H_3V_{10}O_{28}]^{3-}$ and the Dawson-Wells anion $[P_2W_{18}O_{62}]^{6-}$, the salts $(ET)_5[H_3V_{10}O_{28}] \cdot 4H_2O$ and $(ET)_{11}[P_2W_{18}O_{62}] \cdot 3H_2O$ resulted and were found to possess metallic conductivity [18, 19]. Finally, Keggin polyoxometalate clusters with

Fe^{III}

the generic formulae $[XZM_{11}O_{39}]^{5-}$ ($XZM_{11} = SiIVCr^{III}$

$Mo_{11}, SiIVW_{11}, PVCoIIW_{11}, PVNiIIW_{11}, PVCuIIW_{11}, PVZnIIW_{11}, PVMnIIW_{11}$ and $PVMnIIMo_{11}$) were combined with ET to make the salts $(ET)_8[XZM_{11}O_{39}]$ ($XZM_{11} =$

$Fe^{III}Cr^{III}$

$SiIVMo_{11}, SiIVW_{11}, PVCoIIW_{11}, PVNiIIW_{11}, PVCuIIW_{11}$ and $PVZnIIW_{11}$) and $(ET)_8n[PVMnIIM_{11}O_{39}]$ ($M = Mo$ or W) [20]. Of these salts, the latter two are the most interesting as the Keggin clusters form a chainlike heteropolyanion during the course of the electrocrystallization [21].

Considering the facility by which TTF derivatives have been combined with polyoxoanion clusters, especially the dianionic Lindquist polyoxometalates, we sought to prepare a hybrid salt that combined this cluster type

with the TTF derivative o-3,4-dimethyltetraethiafulvalene (o-Me₂TTF) (Fig. 1). This member of the TTF family has been used by the groups of Dunbar and Fourmigue' as a starting material to prepare the redox active chelating diphosphine o-P2 used in various homoleptic transition metal coordination compounds [22-28]. Prior to 2007, the only salt of o-Me₂TTF known was (o-Me₂TTF)[ReO₄]

reported in 1993 where it was oxidized to the +1 oxidation state [29]. Later, the crystal structure of the neutral donor was published in 1998 [30]. In 2008, Fourmigue' et al. [31] reported the structures and properties of a series of isostructural, tetragonal 2:1 salts with the halides Cl⁻, Br⁻ and

I

which possessed metallic conductivity at room temperature. In 2008 and 2009, Reinheimer et al. [32-34] published separate communications describing the syntheses and structural properties of the salts (o-Me₂TTF)[I₃], (o-Me₂TTF)[BF₄] and (o-Me₂TTF)₂[Re₂Cl₈] where like the [ReO₄]⁻ salt, the o-Me₂TTF donor exists as its singly oxidized radical cation. Two years later in 2010, Reinheimer and coworkers reported the 1:1 complex o-Me₂TTF-TCNB (TCNB = 1,2,4,5-tetracyanobenzene), which emphasized the complex's hydrogen bonding network [35].

Herein we present the structure of the hybrid salt (o-Me₂TTF)₂[W₆O₁₉] which combines the unsymmetrical TTF derivative o-Me₂TTF with the closed shell Lindquist polyoxometalate [W₆O₁₉]²⁻. This structure, together with its single crystal IR and Raman spectroscopy data, are useful for evaluating the o-Me₂TTF oxidation state through comparison to theoretical calculations of IR and Raman active modes.

Experimental Section

Preparation of Compounds

For the preparation of the title compound, crystals formed on platinum electrodes of dimensions 1 mm in diameter and 2 cm in length in the anodic compartment of a standard electrochemical H-cell under low constant current [36]. The organosulfur donor o-Me₂TTF and the polyoxoanion (TBA)₂[W₆O₁₉] were prepared via published techniques [37, 38]. The solvent CH₃CN, used in the electrochemical reactions, was not dried prior to its use.

(o-Me₂TTF)₂[W₆O₁₉]

Into both compartments of a standard electrochemical H-cell, (TBA)₂[W₆O₁₉] (0.107 g, 0.057 mmol) was added and dissolved in 10 mL of CH₃CN. The donor o-Me₂TTF (0.0096 g, 0.041 mmol) was combined with the electrolyte

H

CH3

SS

SS

H

CH3

Fig. 1 o-Me2TTF

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solution in the anodic compartment and exposed to a constant current density of 1.0 lA to yield black block-like crystals on the electrode surface which were harvested after a period of 2 weeks, washed with CH₃CN, and dried in air.

X-ray Crystallographic Details and Structure Solution

Diffraction quality crystals were grown on the surface of platinum electrodes by slow anodic oxidation of o-Me₂TTF in the presence of electrolytic solutions of (TBA)₂[W6O19] dissolved in CH₃CN. A black, block-like crystal of dimensions 0.20 × 0.10 × 0.06 mm³ was secured to a glass fiber using paratone oil and placed into the cold gaseous nitrogen stream of a Bruker APEX II diffractometer using Mo-K α radiation ($k = 0.71073 \text{ \AA}^\circ$) at $110 \pm 2 \text{ K}$. All data collections were conducted using graphite monochromated radiation and were corrected for Lorentz and polarization effects. Data collection and initial indexing were handled using SMART [39]. Frame integration, Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT [40]. Multi-scan absorption corrections were performed using SADABS [41]. The space group $P\bar{1}$ was unambiguously assigned by analysis of symmetry and systematic absences using XPREP and further verified by PLATON [42, 43]. The structure was solved using Patterson methods and difference Fourier techniques. The final structural refinement included anisotropic temperature factors on all non-hydrogen atoms, with the exception of atoms C4 and O10 which could not be satisfactorily refined anisotropically. Structure solution, refinement, graphics, and creation of publication material were performed using SHELXS, SHELXL and XSEED [44–46]. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. The solid state structure with anisotropic displacement ellipsoids at 50 % probability is shown in Fig. 2. The central C=C bond and C-S bonds of o-Me₂TTF are the most susceptible to its oxidation state and have been used by Coppens and coworkers [47] to develop an empirical relationship that can be used to calculate the overall oxidation state of the donor molecules. Information regarding refinement details and bond distances for (o-Me₂TTF)₂[W6O19] as well as calculated average changes for the o-Me₂TTF donor in the title salt and other materials are listed in Tables 1–3. CCDC file 890234 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Single Crystal Spectroscopic Studies

Raman spectra within the wavenumber range 50–3,500 cm⁻¹ were measured on single crystals of (o-Me₂TTF)₂[W6O19]

using backscattering geometry. The measurements at room temperature were performed on a Labram Horiba Jobin Yvon 800 spectrometer equipped with He-Ne laser (632.8 nm) and

a liquid-nitrogen cooled CCD detector. To avoid sample overheating and possible decomposition, the power of the exciting laser beam was reduced to ~ 0.1 mW. The electrical vector of the exciting laser beam was nearly parallel and perpendicular to the maximum measured intensity for the C=C stretching vibrations of o-Me₂TTF, individual molecules of which were aggregated into dimers, approximately perpendicular ($E \perp a$) and parallel ($E \parallel a$) to the crystallographic a-axis.

Fig. 2 (a) View of the unit cell of (o-Me₂TTF)₂[W₆O₁₉] illustrating the tendency of the o-Me₂TTF radical cations to form face-to-face dimers in the solid state. (b) Detail of the face-to-face overlap between cation radicals. (c) Chain of dimers running along the a axis. The atoms are drawn with van der Waals radii

Table 1 X-ray crystallographic and refinement data for (o-Me₂TTF)₂[W6O19]

Compound (o-Me₂TTF)₂[W6O19]

CCDC code 890234

Formula C₁₆H₁₆S₈W₆O₁₉

Formula weight 1871.51

Temp. 110(2)

Space group P1

a, 7.6211(7)

°

b, 9.5231(9)

°

c, 12.2148(11)

°

a, .

105.5870(10)

b, .

106.8340(10)

c, .

95.6950(10)

°³

Volume, 802.10(13)

Z1

Density (calculated), mg/m³ 3.845

l, mm⁻¹ 22.026

Scan x scan

h range for data collection, .

1.83–28.66

Reflections measured 4092

Independent observed reflns. 3707

Independent reflns. [I [2r] 3613

Data/restraints/parameters 3707/0/216

Rint 0.0296

Final R indices [I [2r] R1 = 0.0222,

wR2 = 0.0550

R indices (all data) R1 = 0.0230,

wR2 = 0.0555

Goodness-of-fit on F² 1.155

2 22]1/2

$R1 = R(|Fo| - |Fc|)/|Fo|$. $wR2 = [R [w(Fo - Fc)^2]/R [w(Fo)^2]$.

)]1/2

Goodness-of-fit = $[Rw(|Fo| - |Fc|)^2/(Nobs - Nparameter$

°

Table 2 Bond distances for (o-Me₂TTF)₂[W6O19] in A

W(1)-O(1) 1.694(4) W(3)-O(8) 1.929(3)
 W(1)-O(2) 1.917(4) W(3)-O(9) 1.706(4)
 W(1)-O(3) 1.928(3) W(3)-O(10) 2.3268(2)
 W(1)-O(6) 1.926(3) S(1)-C(1) 1.721(5)
 W(1)-O(8) 1.920(3) S(1)-C(2) 1.714(5)
 W(1)-O(10) 2.3243(2) S(3)-C(4) 1.706(5)
 W(2)-O(2) 1.910(4) S(3)-C(6) 1.736(5)
 W(2)-O(4) 1.922(3) S(4)-C(4) 1.718(5)
 W(2)-O(5) 1.709(4) S(4)-C(7) 1.739(5)
 W(2)-O(6) 1.931(3) C(1)-C(4) 1.391(6)
 W(2)-O(7) 1.924(3) C(2)-C(3) 1.332(8)
 W(2)-O(10) 2.3221(3) C(5)-C(6) 1.502(7)
 W(3)-O(3) 1.910(3) C(6)-C(7) 1.336(7)
 W(3)-O(4) 1.931(3) C(7)-C(S) 1.499(7)
 W(3)-O(7) 1.911(3)

Polarized reflectance spectra were measured from the bestdeveloped crystal face of single crystals (700-16,000 cm⁻¹). The spectra were measured for various polarizations of the incident IR beam, which corresponded to maximum and minimum measured intensities of the electronic band at 10,800 cm⁻¹ with electrical vector orientations nearly parallel or perpendicular to the (o-Me₂TTF)₂ stacking axis. The spectra were recorded using a Bruker Equinox 55 FT-IR spectrometer equipped with a Bruker microscope Hyperion 1000. The reflectance data were normalized to the reflectance of a high quality aluminum mirror.

Results and Discussion

X-Crystallography

The solid-state structure for (o-Me₂TTF)₂[W₆O₁₉] represents the first charge-transfer salt between the donor o-Me₂TTF and the dianionic, diamagnetic Lindquist polyoxoanion [W₆O₁₉]²⁻. It has been well established by our group and others that in the absence of any intermolecular contacts such as p-p or S...S interactions, neutral chalcofulvalene donors are nonplanar, often exhibiting significant bends of up to 30° along dithiole or diseleno bridges [22-28]. The solid-state structures of neutral tetrathiafulvalene-based molecules are often controlled by weak van der Waals forces. These interactions define the molecular shape, size, and close packing properties in the solid-state and govern the formation of different patterns of association such as the herringbone conformation in a TTF polymorph and the sandwich herringbone pattern of dimers in the structure of neutral BEDT-TTF [48, 49].

Upon oxidation of the o-Me₂TTF donor, structural changes in the molecule occur, including the adoption of a planar conformation followed by a lengthening of the central C=C bond and a shortening of the C-S bonds in the central TTF core [50-60]. Using the Coppens' formula, the oxidation state for the o-Me₂TTF donors was confirmed to be 1; this was further confirmed upon comparison of

the central C=C and mean C-S bond distances from (o-Me₂TTF)₂[W₆O₁₉] to those for other materials known to contain oxidized o-Me₂TTF moieties [29-34, 47].

For the title salt, the o-Me₂TTF donors exist as strong face-to-face dimers of their corresponding radical cations (Fig. 2a). While this was surmised on the basis of calculation using the Coppens' formula and direct comparison to other o-Me₂TTF-containing materials, this aggregation into dimers within the solid state also furnishes a structural indicator. In previous cases of TTF and its derivatives with the dianionic Lindquist polyoxoanions published to date, most salts contain donors in the +1 oxidation state [8-13]. In those and other cases where radical cations of chalcophthalene donors

Table 3 Estimated degree of

Salt Molecule Aa (A°) Bb (A°) Qc References

ionicity for the o-Me₂TTF

donor in (o-Me₂TTF)₂[W6O19]

o-Me₂TTF A

and its comparison to other

o-Me₂TTF-TCNB A

calculated valences for

published o-Me₂TTF-containing (o-Me₂TTF)₂[I] A
materials

A

(o-Me₂TTF)[ReO₄] A

(o-Me₂TTF)[I₃] A

a Central C=C bond distance

b(o-Me₂TTF)[BF₄] A

Mean central C-S bond

(o-Me₂TTF)₂[Re₂Cl₈] A

distance

cB

Q =charge estimated

with the formula (o-Me₂TTF)₂[W6O19] A

Q =-17.92 ?23.43 9

A

(A/B) from Ref. [43]

are present, according to a review by Fourmigue' and Batail [61], the radicals form strong face-to-face dimers with short interatomic distances between their chalcogen atoms being less than the sum of the van der Waals radii. This eclipsed face-to-face interaction between radical cations corresponds to the formation of r-bonding and r*-antibonding combinations of the two SOMOs, a dispersion of molecular orbitals fundamentally equivalent to that seen for diatomic hydrogen. As each SOMO contributes a single electron to the r-bonding MO, a strong r bond occurs between the radicals ultimately resulting in charge localization and insulating properties. A projection in the (111) plane illustrating the formation of the strong, eclipsed face-to-face interactions is presented in Fig. 2b. The head-to-tail orientation of the o-Me₂TTF radicals for (o-Me₂TTF)₂[W6O19] is similar to that seen in (o-Me₂TTF)[I₃], (o-Me₂TTF)[BF₄] and

(o-Me₂TTF)[ReO₄], but is different from the orientation found in (o-Me₂TTF)₂[Re₂Cl₈] where a head-to-head orientation of radicals is observed [32–34].

Commencing with the unit cell, a dimer containing o-Me₂TTF radicals was found to be nearly parallel to the ab plane, others can be generated through translations in all directions. For translations along the b- and c-axes, the dimers are effectively separated by the void containing the [W₆O₁₉]₂-polyoxometalate. The polyoxoanion itself is centrally located within the ac plane and related to other symmetry generated polyoxoanions through translations in all three dimensions. Structural features of the [W₆O₁₉]₂polyoxoanion from (o-Me₂TTF)₂[W₆O₁₉] are consistent with those observed previously in other TTF-based salts utilizing this anion [8–14].

For o-Me₂TTF radical dimers related by translations along the a-axis, their stacking is reminiscent of a stair-step pattern and reveals no close interatomic interactions between neighboring sulfur atoms at distances $\sim 3.6 \text{ \AA}$ (Fig. 2c). Despite appearing that there may be long range interactions between sulfur atoms along the a-axis, there is no satisfactory long range stacking between the oxidized

1.340(4) 1.762(3) 0 [30]
1.342(7) 1.755(2) 0 [33]
1.365(5) 1.738(4) ~ 0.48 [31]
1.365(5) 1.738(4) ~ 0.48
1.39(1) 1.716(5) ~ 1.06 [29]
1.401(5) 1.722(4) ~ 1.14 [32]
1.386(4) 1.721(2) ~ 0.95 [33]
1.401(3) 1.715(3) ~ 1.22 [34]
1.373(2) 1.717(4) ~ 0.82
1.391(5) 1.716(4) ~ 1.07 This study
1.391(5) 1.716(4) ~ 1.07

o-Me₂TTF moieties which could lead to either activated or non-activated conductivity as short intradimer ($\sim 3.6 \text{ \AA}$)

and longer interdimer ($\sim 3.6 \text{ \AA}$) interactions exist in an alternating pattern involving the o-Me₂TTF radicals and successive dimers respectively along a.

Among the solid structure for (o-Me₂TTF)₂[W₆O₁₉], hydrogen bonding interactions, which can be suggested if interatomic distances between oxygen and hydrogen atoms are $\sim 2.70 \text{ \AA}$ (the sum of their corresponding van der Waals radii), were found between hydrogen atoms bound to sp²-hybridized carbon atoms from o-Me₂TTF and the bridging oxygen atoms of the [W₆O₁₉]₂-polyoxoanion clusters. A 1999 report by Batail and coworkers [62] demonstrated, by the use of electrostatic potential maps, that bridging oxygen atoms in these clusters are more basic and thus better hydrogen bond acceptors than those in terminal positions. Within our structure (Fig. 3), short Csp²-H \cdots O interactions of 2.296 and 2.512 \AA exist between H8–O9 and H7–O4 respectively within the (111) plane. In

both cases, a bridging oxygen atom from the tungsten cluster acts as a hydrogen bonding acceptor. While other interactions between hydrogen and oxygen atoms at distances $\sim 2.70 \text{ \AA}$ were found, their close approximation (within $\pm 0.03\text{--}0.07 \text{ \AA}$) to the threshold value of 2.70 \AA makes their identification as actual hydrogen bonding interactions problematic. The fact that the observed Csp²-H \cdots O interactions are well below the threshold value of

°

2.70 \AA and involve bridging oxygen atoms from the [W₆O₁₉]²⁻ cluster, provides structural support that those particular oxygen atoms from the cluster, with their elevated basicity, are better hydrogen bond acceptors than their terminal counterparts.

Single Crystal Spectroscopic Properties

In previous spectroscopic measurements on o-Me₂TTF containing materials, particularly the neutral donor and the

2:1 salts (o-Me₂TTF)₂[X] (X = Cl⁻, Br⁻ and I⁻) where

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Fig. 3 Detail of the hydrogen bond pattern (see text). Anisotropic displacement ellipsoids have been set to 50 % probability

o-Me₂TTF bears a $\pm 1/2$ charge, IR and Raman spectra were successfully measured [63]. During the course of those studies, the normal vibrational modes of the neutral and the radical cation, as well as their theoretical IR and Raman spectra, were calculated by quantum chemical methods. Utilizing these theoretical calculations, experimentally observed vibrational features of o-Me₂TTF were assigned [63]. For (o-Me₂TTF)₂[W6O19], the solid state structure reveals that each donor molecule bears a ± 1 charge and aggregates with other o-Me₂TTF radical cations to form isolated dimers. Upon consideration of the structural features of the (o-Me₂TTF)₂[W6O19] salt, the isolated dimer model can be used to explain the features of the spectra. In this model, one can distinguish two dimeric modes: the in-phase vibration of monomers, which is Raman active, and the out-of-phase mode, which is IR active due to coupling with the electronic transition.

The Raman spectra of the title salt are displayed in Fig. 4 for two polarizations of the incident laser beam which were nearly parallel and perpendicular to the stacking axis of the o-Me₂TTF radical cations in the isolated dimers, that being the crystallographic a-axis. For perpendicular polarization, the strongest bands for o-Me₂TTF[±] are attributed to the C=C stretching modes ($m_9 = 1,556 \text{ cm}^{-1}$, $m_{10} = 1,483 \text{ cm}^{-1}$, $m_{11} = 1,417 \text{ cm}^{-1}$) and the ring breathing mode ($m_{38} = 518 \text{ cm}^{-1}$) [63]. These experimental data compare closely with those stretches determined theoretically: $m_9 = 1,603 \text{ cm}^{-1}$, $m_{10} = 1,546 \text{ cm}^{-1}$, $m_{11} = 1,436 \text{ cm}^{-1}$, $m_{38} = 482 \text{ cm}^{-1}$ [63]. In the spectrum we also find some other bands related to the o-Me₂TTF radical cations: $m_{20} = 1,101 \text{ cm}^{-1}$ (C-H bend), $m_{21} = 1,036 \text{ cm}^{-1}$ (C-C stretch), $m_{25} = 975 \text{ cm}^{-1}$ (C-S stretch), $m_{26} = 937 \text{ cm}^{-1}$ (C-S stretch, C-C stretch), $m_{31} = 754 \text{ cm}^{-1}$ (rock CH₃), $m_{32} = 720 \text{ cm}^{-1}$ (C-S stretch), $m_{34} = 627 \text{ cm}^{-1}$ (in-plane deformation), $m_{40} = 473 \text{ cm}^{-1}$ (ring breath), $m_{45} = 274 \text{ cm}^{-1}$ (in-plane deformation), $m_{47} = 234 \text{ cm}^{-1}$ (out-of-plane deformation) [63]. The anion W6O19²⁻ has 11 Raman active modes [64]. In the spectrum of (o-Me₂TTF)₂[W6O19] we observe 7 bands assigned to W6O19²⁻-anions: $m_1(\text{alg}) = 995 \text{ cm}^{-1}$, $m_6(\text{eg}) = 968 \text{ cm}^{-1}$, $m_7(\text{eg}) = 830 \text{ cm}^{-1}$, $m_2(\text{alg}) = 555 \text{ cm}^{-1}$, $m_8(\text{eg}) = 501 \text{ cm}^{-1}$, $m_3(\text{alg}) = 228 \text{ cm}^{-1}$ and

500 1000 1500 2000
0
500
1000
1500
0
1000
2000
3000

```

4000
5000
6000
7000
[o-DMTTF]2W6O19
E aIntensityT
141714831556
E II aIntensity
[o-DMTTF]2W6O19
141714831556
518518
Raman Shift [cm-1]

```

Fig. 4 Raman spectrum of (o-Me₂TTF)₂[W6O19] obtained with a red excitation (632.8 nm) for two perpendicular polarizations of the laser beam

m₉(eg) = 181 cm⁻¹. These wavenumbers agree quite well with those reported in Reference 64.

It is well-known that the C=C modes of TTF derivatives are very sensitive to the degree of oxidation and as such are often used for the determination of charge density distribution [47]. Based on the behavior of these modes for charge transfer salts of TMTTF, ET and bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF), their C=C bond frequencies depend linearly (or nearly linearly) on charge density. When the average oxidation state grows, the wavenumber for the C=C modes decreases considerably by *60-110 cm⁻¹ per ?1 charge. For the title salt, a similar nearly linear charge dependency was observed for the analogous C=C modes of the o-Me₂TTF donor and is represented within Fig. 5 where we outline the spectral response for selected Raman active bands for o-Me₂TTF₀, o-Me₂TTF_{0.5} and the present data for o-Me₂TTF₁. Concurrently, when the donor's oxidation state increases, the ring breathing mode, m₃₈, shifts towards higher wavenumbers (*23 cm⁻¹ per ?1 charge). Such spectroscopic behavior is equivalent to that seen for other TTF derivatives [65-67].

The polarized reflectance spectrum for (o-Me₂TTF)₂[W6O19] is shown in Fig. 6 for polarizations parallel (E||a)

1650

towards lower wavenumbers because of the e-mv coupling effect. Similar shift patterns were also observed for charge transfer salts containing other TTF derivatives, thus pro

1600

viding evidence suggesting strong electronic coupling. In the IR spectrum we also find two bands related to C-S

0.0 0.5 1.0

.11

.10

.9

stretching modes: the m25 mode at 988 cm⁻¹ (E||a) activated by e-mv coupling and the IR active m30 mode at 795 cm⁻¹

1550

Wavenumber (cm⁻¹)

observed for both polarizations (779 cm⁻¹ for neutral

1500

o-Me₂TTF [63]). Additionally, in the reflectance spectrum we observe 3 bands assigned to the [W6O19]²⁻ anion:

m14(tlu) = 972 and 966 cm⁻¹ (doublet), m15(tlu) = 830 cm⁻¹

1450

and m16(tlu) = 576 cm⁻¹ [64]. The dimer model originally developed for K-TCNQ and later applied to (ET)₂[Mo6O19],

1400

provided reliable estimates of electron-molecular coupling constants for TCNQ⁻ and BEDT-TTF⁺, respectively [68,

Charge (+e)

69]. Analogously, the IR spectra for (o-Me₂TTF)₂[W6O19]

Fig. 5 Frequencies of the C=C stretching modes of o-Me₂TTF

can be used for determination of electron-molecular coupling molecule versus ionization degree

constants for the o-Me₂TTF⁺.

0.0

0.1

0.2
 0.3
 0.4
 0.5
 0.6
 0.7
 0.8
 0.9
 0.0
 0.1
 0.2
 0.3
 0.4
 0.5
 0.6
 0.7
 0.8
 0.9
 1.0
 [o-DMTTF]2W6O19
 E aReflectanceT
 806966
 E II aReflectance[o-DMTTF]2W6O19
 1350795988
 1000 2000 3000 5000 10000 15000

Conclusions

Herein we describe the X-ray crystallographic structure and spectroscopic properties of the hybrid charge transfer salt (o-Me2TTF)2[W6O19] which contains radical cations of the unsymmetrical TTF derivative o-Me2TTF and the closed shell Lindquist polyoxometalate [W6O19]2-. Close inspection of the structure revealed isolated dimers of o-Me2TTF radical cations encompassing strong face-to-face overlap and intradimer S...S interactions between neighboring sulfur atoms at distances $\sim 3.6 \text{ \AA}$. These

Wavenumber [cm⁻¹]

Fig. 6 Reflectance spectrum of (o-Me2TTF)2[W6O19] salt for two perpendicular polarizations, corresponding to maximum (E||a) and minimum (E⊥a) intensity of the electronic transition at 10,800 cm⁻¹

and perpendicular (E⊥a) to the dimer axis. For polarization nearly parallel to the dimer axis, we observe an electronic band at $\sim 10,800 \text{ cm}^{-1}$, corresponding to an intradimer charge transfer transition. This band is a characteristic feature of the salts containing dimers of TTF-type radical cations; for example, in (ET)2[Mo6O19] and (DMtTTF)[Br], this band was located at 7,000 and 8,300 cm⁻¹ respectively [68]. It is remarkable that in (o-Me2TTF)2[W6O19], this electronic transition is located at higher frequency, i.e. the interaction between the o-Me2TTF radical cations within the dimer is smaller. The relatively strong vibrational feature at 1,350 cm⁻¹ (E||a) is related to the effect of electron-molecular vibration (e-mv) coupling of the m11 mode (C=C central bond stretching) with the

charge-transfer transition. In comparison with the analogous Raman band, this IR feature is shifted by 67 cm⁻¹

structural features are strongly indicative of regions of charge localization which ultimately result in insulating properties. Hydrogen bonds between bridging oxygen atoms of the polyoxometalate cluster and the o-Me₂TTF radicals were also observed at distances well below the threshold value of 2.70 Å. As these interactions involve the bridging oxygen atom of the cluster, it supports the computationally-determined hypothesis that bridging oxygen atoms of polyoxometalate clusters, with their heightened basicity, are better hydrogen bond acceptors than their terminal analogues. Single crystal spectroscopic studies were also completed on the IR and Raman active modes of the oxidized o-Me₂TTF donor. Identification and analysis of these modes correlate with theoretical spectra for o-Me₂TTF^{•+} determined using quantum chemical methods. The frequency change for the C=C mode in o-Me₂TTF with respect to oxidation state follows a linear (or nearly linear) trend as seen for other TTF derivatives. Finally, a strong intradimer charge transfer transition was observed at *10,800 cm⁻¹, which is indicative of the dimerization of TTF-type radical cations in the solid state. The title salt adds another 2:1 phase to the library of salts containing

TTF derivatives and the [W6O19]2-anion and provides IR and Raman stretches for the o-Me₂TTF donor in its radical cation form, spectral information important for continuing studies on complexes containing this organic donor.

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References

1. Coronado E, Day P (2004) Chem Rev 104:5419
2. Ferraris J, Cowan DO, Walatka VJ, Perlstein JH (1973) J Am Chem Soc 95:948
3. Bechgaard K, Jacobsen CS, Mortensen K, Pedersen HJ, Thorup N (1980) Solid State Commun 33:1119
4. Williams JM, Ferraro JR, Thorn RJ, Carlson KD, Geiser U, Wang HH, Kini AM, Whangbo M-H (1992) Organic superconductors. Prentice Hall, Englewood Cliffs
5. Kurmoo M, Graham AW, Day P, Coles SJ, Hursthouse MB, Caulfield JL, Singleton J, Pratt FL, Hayes W, Ducasse L, Guineau P (1995) J Am Chem Soc 117:12209
6. Coronado E, Gala'n-Mascaro's JR, Go'mez-Garcia CJ, Laukhin V (2000) Nature 408:447
7. Coronado E, Go'mez-Garci'a CJ (1998) Chem Rev 98:273
8. Triki S, Ouahab L, Padiou J, Grandjean D (1989) J Chem Soc Chem Commun 1068
9. Bellitto C, Attanasio D, Bonamico M, Fares V, Imperatori P, Patrizio S (1990) Mater Res Soc Symp Proc 173:143
10. Triki S, Ouahab L, Grandjean D (1991) Acta Crystallogr C47:645
11. Coronado E, Gala'n-Mascaros JR, Gime'nez-Saiz C, Go'mezGarci'a CJ, Rovira C, Tarre's J, Triki S, Veciana J (1998) J Mater Chem 8:313
12. Triki S, Ouahab L, Grandjean D, Amiel J, Garrigou-Lagrange C, Delhaes P, Fabre JM (1991) Synth Met 42:2589
13. Triki S, Ouahab L (1993) Acta Crystallogr C49:132–135
14. Reinheimer EW, Fourmigue' M, Dunbar KR (2009) J Chem Crystallogr 39:723
15. Triki S, Ouahab L, Halet JF, Pen~a O, Padiou J, Grandjean D, Garrigou-Lagrange C, Delhaes P (1992) J Chem Soc Dalton Trans 1217
16. Triki S, Ouahab L, Grandjean D (1991) Acta Crystallogr C49:132
17. Triki S, Ouahab L, Grandjean D, Canet R, Garrigou-Lagrange C, Delhaes P (1993) Synth Met 55–57:2028
18. Coronado E, Ga'lan-Mascaro's JR, Gime'nez-Saiz C, Go'mezGarci'a CJ, Marti'nez-Ferrero E, Almeida M, Lopes EB (2004) Adv Mater 16:324
19. Coronado

E, Ga'lan-Mascaro's JR, Gime'nez-Saiz C, Go'mezGarci'a CJ, Laukhin VN (1996) Adv Mater 8:801

20. Coronado E, Ga'lan-Mascaro's JR, Gime'nez-Saiz C, Go'mezGarci'a CJ, Triki S (1998) J Am Chem Soc 120:4671

21. Ga'lan-Mascaro's JR, Gime'nez-Saiz C, Triki S, Go'mez-Garci'a CJ, Coronado E, Ouahab L (1995) Angew Chem Int Ed Engl 34:1460

22. Fourmigue' M, Uzelmeier CE, Boubekur K, Bartley SL, Dunbar KR (1997) J Organomet Chem 529:343

23. Smucker BW, Dunbar KR (2000) Dalton Trans 1309

24. Uzelmeier CE, Smucker BW, Reinheimer EW, Shatruk M, O'Neal A, Fourmigue' M, Dunbar KR (2006) Dalton Trans 5259

25. Avarvari N, Fourmigue' M (2004) Chem Commun 1300

26. Avarvari N, Martin D, Fourmigue' M (2002) J Organomet Chem 643-644:292

27. Gouverd C, Biaso F, Cataldo L, Berclaz T, Geoffroy M, Levillain E, Avarvari N, Fourmigue' M, Sauvage FX, Wartelle C (2005) Phys Chem Chem Phys 7:85

28. Kobayashi A, Fujiwara E, Kobayashi H (2004) Chem Rev 104:5243

29. Mhanni A, Ouahab L, Grandjean D, Amoroux J, Fabre JM (1993) Acta Crystallogr C49:1187

30. Uzelmeier CE, Fourmigue' M, Dunbar KR (1998) Acta Crystallogr C54:1047

31. Fourmigue' M, Reinheimer EW, Dunbar KR, Auban-Senzier P, Pasquier C, Coulon C (2008) Dalton Trans 4652

32. Reinheimer EW, Fourmigue' M, Dunbar KR (2009) J Chem Crystallogr 39:735

33. Reinheimer EW, Zhao H, Dunbar KR (2008) Synth Met 158:447

34. Reinheimer EW, Gala'n-Mascaro's JR, Go'mez-Garci'a CJ, Zhao H, Fourmigue' M, Dunbar KR (2008) J Mol Struct 890:81

35. Reinheimer EW, Zhao H, Dunbar KR (2010) J Chem Crystallogr 40:514

36. Batail P, Boubekur K, Fourmigue' M, Gabriel JCP (1998) Chem Mater 10:3005

37. Che M, Fournier M, Launay JP (1979) J Chem Phys 71:1954

38. Gerson F, Lamprecht A, Fourmigue' M (1996) J Chem Soc Perkin Trans 2:1409

39. SMART (1998) Software for the CCD detector system, version 5.050 (NT). Bruker Analytical X-ray Systems, Madison

40. SAINT (1998) Software for the CCD detector system, version 5.01 (NT). Bruker Analytical X-ray Systems, Madison

41. Blessing RH (1995) SADABS, program for absorption corrections using Siemens CCD based on the method of Robert Blessing. Acta Crystallogr A 51:33

42. Sheldrick GM (1996) XPREP, program for space group determination. University of Go'ttingen, Go'ttingen

43. Speck AL (2001) PLATON, a multipurpose crystallographic tool. Utrecht University, Utrecht

44. Sheldrick GM (1997) SHELXS-97, program for crystal structure determination. University of Go'ttingen, Go'ttingen

45. Sheldrick GM (1997) SHELXL-97, program for the crystal structure refinement. University of Go'ttingen, Go'ttingen

46. Barbour LJ (2001) J Supramol Chem 1:189

47. Umland TC, Allie S, Kuhlmann T, Coppens P (1987) J Phys Chem 92:6456
48. Ellern A, Bernstein J, Becker JY, Zamir S, Shalal L, Cohen S (1994) Chem Mater 6:1378
49. Cooper WF, Edmonds JW, Wudl F, Coppens P (1974) Cryst Struct Commun 3:23
50. Alberola A, Coronado E, Gala'n-Mascaro's JR, Gime'nez-Saiz C, Go'mez-Garci'a CJ (2003) J Am Chem Soc 125:10774
51. Coronado E, Gala'n-Mascaro's JR, Go'mez-Garci'a CJ, MurciaMartinez A, Canadell E (2004) Inorg Chem 43:8072
52. Coronado E, Gala'n-Mascaro's JR, Go'mez-Garci'a CJ, Marti'nez-Ferrero E, van Smaalen S (2004) Inorg Chem 43:4808
53. Clemente-Leo'n M, Coronado E, Gala'n-Mascaro's JR, Gime'nez-Saiz C, Go'mez-Garci'a CJ, Ribera E, Vidal-Gancedo J, Rovira C, Canadell E, Laukhin V (2001) Inorg Chem 40:3526
54. Clemente-Leo'n M, Coronado E, Gala'n-Mascaro's JR, Gime'nez-Saiz C, Go'mez-Garci'a CJ, Rovira C, Laukhin VN (1999) Synth Met 103:2339
55. Clemente-Leo'n M, Coronado E, Gala'n-Mascaro's JR, Gime'nez-Saiz C, Go'mez-Garci'a J, Fabre JM (1999) Synth Met 103:2279
56. Kobayashi H, Tomita H, Naito T, Kobayashi A, Sakai Watanabe T, Cassoux P (1996) J Am Chem Soc 118:368
57. Bousseau M, Valade L, Legros JP, Cassoux P, Garbaskas M, Interrante LV (1986) J Am Chem Soc 108:1908

J Chem Crystallogr (2013) 43:178–186

58. Perruchas S, Boubekeur K, Auban-Senzier P (2004) J Mater Chem 14:3509
59. Kazheva ON, Alexandrov GG, Dyachenko OA, Zinenko TN, Kravchenko AV, Starodub VA, Khotkevich AV (2006) Synth Met 156:251
60. Chi X, Scott B, Lawes G, Ramirez AP (2004) J Chem Crystallogr 34:249
61. Fourmigue´ M, Batail P (2004) Chem Rev 104:5379
62. Dolbecq A, Guirauden A, Fourmigue´ M, Boubekeur K, Batail P, Rohmer MM, Be´nard M, Salle´ M, Blanchard P (1999) J Chem Soc Dalton Trans 1241

Raman Spectr 42:1518

63. Jankowski D, S wietlik R, Reinheimer EW, Fourmigue´ M (2011) J
64. Bridgeman AJ, Cavigliasso G (2002) Chem Phys 279:143
65. Meneghetti M, Bozio R, Zanon I, Pecile C, Ricotta C, Zanetti M (1984) J Chem Phys 80:6210
66. Yamamoto T, Uruichi M, Yamamoto K, Yakushi K, Kawamoto A, Taniguchi H (2005) J Phys Chem B 109:15226
67. Drozdowa O, Yamochi H, Yakushi K, Uruichi M, Horiuichi S, Saito G (2000) J Am Chem Soc 122:4436
68. Visentini G, Masino M, Bellitto C, Girlando A (1998) Phys Rev B 58:9460
69. Rice MJ, Lipari NO, Stra¨ssler S (1977) Phys Rev Lett 39:1359
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