Synthesis, Crystal Structure, and Spectral Characterization of Novel Three-dimensional Supramolecular Networks with One-dimensional Channels Based on Keggin-type Polyoxoanions and Mixed-Valence Dibenzotetrathiafulvalenes

Dongmei Shi^a, Yaguang Chen^a, Haijun Pang^a, Fanxia Meng^a, Yu Sun^a, Kun Liu^a, and Hongbo Liu^{a, b}

^a Key Laboratory of Polyoxometalates, Science of Ministry of Education, College of Chemistry, Northeast Normal University, Changchun 130024, P.R. China

^b Department of Pharmaceutics, Changchun Medical College, Changchun 130031, P.R. China

Reprint requests to Dr. Yaguang Cheng. E-mail: chenyg146@nenu.edu.cn

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A new organic/inorganic salt formed by mixed-valence dibenzotetrathiafulvalene (DBTTF) radical cations and the spherical Keggin-type polyoxometalate anions $[H_3BW_{12}O_{40}]^{2-}$ was obtained by electrochemical oxidation of the donor in an acetonitrile and a 1,2-dichloroethane solution containing the polyanion. The compound has been characterized by X-ray diffraction, elemental analysis, EPR, IR and Raman spectroscopy. X-Ray diffraction experiments have revealed that the compound consists of heteropolyanions, water molecules and DBTTF radical cations. The organic radicals form trimers and dimers *via* π - π stacking; moreover, the polyoxoanions and the organic donors are also held together by hydrogen bonding interactions. In their packing arrangement, a three-dimensional supramolecular network with one-dimensional channels along the *b* axis is established with uncoordinated water molecules residing in the channels.

Key words: Radical Cation Salts, Electrochemical Oxidation, Polyoxometalate, DBTTF, Supramolecular

Introduction

There is considerable current interest in the preparation of compounds constructed from two molecular networks as they provide a source of novel materials with highly anisotropic electrical, optical and magnetic properties [1-6]. Many polyoxometalates (POMs) have well-defined sizes and fascinating shapes as well as the ability to undergo multiple electron reductions [7], which make the POMs attractive precursors for the preparation of new radical-ion salts based on π -electronic organic donors of the tetrathiafulvalene-type (in short TTF) and their derivatives with magnetic counterions [8]. Therefore, a number of organic/inorganic hybrid materials based on conducting organic donors and POMs have been reported [4, 9].

However, these compounds usually crystallize in two-dimensional (2D) layers of conducting donors alternating with insulating layers of anions. Up to now, the process of assembling POMs into 3D supramolecules is still in its infancy [10]. Furthermore, porous supramolecular compounds containing Keggin frameworks have rarely been reported [11, 12], especially with TTF and its derivatives. Herein, we have chosen the Keggin cluster $[H_3BW_{12}O_{40}]^{2-}$ as the building block for two main reasons: (i) it has high charge density [13]; (ii) the activity of the terminal oxygen atoms on the surface makes it possible to form 3D supramolecules under appropriate reaction conditions.

In this context, we present for the first time the synthesis, structure and physical properties of the DBTTF radical cation salts associated with $[H_3BW_{12}O_{40}]^{2-}$. The organic radical cations and the polyoxoanions are joined together by hydrogen bonding interactions to form a 3D supramolecular network with 1D channels, in which interstitial water molecules reside.

Results and Discussion

Crystal structure description and discussion

The exact stoichiometry 7:2 formed by DBTTF and polyoxometalate components, as well as the number of water molecules of compound **1** were determined by

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Fig. 1. Left: ORTEP drawing of the components of 1 with thermal ellipsoids at the 50% probability level. Right: View of the unit cell content in the *ab* plane. The water molecules and the H atoms are omitted for clarity.



Fig. 2. View of the alternating layers of **1** showing the DBTTF units and water molecules.

refinement of the crystal structure (Fig. 1), which is different from that observed in DBTTF salts with the Keggin polyoxoanion (DBTTF)₆HSiMo₁₂O₄₀ \cdot 4H₂O [14].

In the crystal, the $[H_3BW_{12}O_{40}]^{2-}$ cluster shows the classic Keggin structure, which consists of a central BO₄ tetrahedron surrounded by four W₃O₁₃ units (Fig. 1 (left)). Each W₃O₁₃ group is composed of three WO₆ octahedra linked in a triangular arrangement by sharing edges. From Tables 1 and 2, it is evident that the $[H_3BW_{12}O_{40}]^{2-}$ cluster is slightly distorted.

The 14 DBTTF molecules of the unit cell belong to three crystallographically non-equivalent types (Fig. 1 and 2), labeled as A, B and C in Fig. 1 (right), of which molecules A and B are aligned along the *c* axis forming an A–B–A trimer, with S1(A)…S3(B) and S2(A)…S3(B) distances of 3.513 and 3.527 Å, respectively. Molecules C are parallel to each other forming dimers along the *a* axis, the S4(C1)…S7(C2) and S5(C1)…S6(C2) distances being 3.299 and 3.416 Å, respectively. Because these distances are shorter than the sum of the van der Waals radii (3.70 Å), it can be assumed that there exist interactions within the trimers and dimers.

The trimers and the water molecules are located alternately along the c axis, while the dimers and the water molecules are located alternately along the a axis. The orientation of the DBTTF molecules in **1** is very different from that in DBTTF molecular crystals and from that in other DBTTF salts [15-17], as well as from that in TTF or BEDT-TTF molecules found in their heteropolyanionic charge transfer salts [18, 19], which are semiconductors or conductors. The alternating arrangement of DBTTF radicals and water clusters in **1** seems to result in poor electrical conductivity.

Table 1. Selected bond lengths (Å) for 1. (Symmetry transformations used to generate equivalent atoms: ^{#1} x, -y, z, ^{#3} -x, -y+2, -z+1).

W(1)-O(1)	1.706(13)	W(3)–O(3)	1.678(15)
W(1)-O(10)	1.899(6)	W(3)-O(16)	1.883(14)
W(1)-O(14)	1.922(15)	W(3)-O(20)	1.914(14)
W(1)-O(19)	1.935(13)	W(3)–O(4)	1.939(10)
W(1)-O(13)	1.942(15)	W(3)–O(15)	1.935(15)
W(1)-O(24)	2.371(13)	W(3)-O(25)	2.323(13)
W(2)–O(2)	1.69(2)	W(5)–O(11)	1.72(3)
W(2)-O(14)	1.858(14)	W(5)-O(17)	1.914(15)
W(2)-O(15)	1.888(15)	W(5)-O(18)	1.911(15)
W(2)-O(25)	2.381(17)	W(5)-O(23)	2.347(19)
W(4)–O(5)	1.703(14)	W(6)–O(8)	1.668(19)
W(4)-O(17)	1.904(17)	W(6)-O(18)	1.892(14)
W(4)-O(21)	1.908(14)	W(6)-O(9)	1.905(6)
W(4)-O(16)	1.919(15)	W(6)–O(13)	1.906(14)
W(4)–O(6)	1.921(10)	W(6)-O(22)	1.929(15)
W(4)-O(23)	2.358(13)	W(6)-O(24)	2.339(15)
W(7)-O(12)	1.691(13)	W(7)-O(19)	1.904(13)
W(7)-O(20)	1.876(14)	W(7)-O(22)	1.870(16)
W(7)-O(21)	1.886(13)	W(7)-O(24)	2.345(12)
B(1)-O(24)	1.533(18)	B(1)-O(25)	1.55(3)
B(1)-O(23)	1.55(3)	S(1)-C(2)	1.74(2)
S(2)–C(1)	1.72(2)	S(1)–C(3)	1.74(2)
S(2)–C(2)	1.75(2)	S(3)–C(8)	1.72(2)
S(4)–C(18)	1.71(2)	S(3)–C(9)	1.79(3)
S(4)–C(16)	1.73(2)	S(5)-C(18)	1.72(2)
S(6)-C(19)	1.72(3)	S(5)–C(15)	1.73(3)
S(6)-C(20)	1.76(2)	S(7)–C(19)	1.68(2)
C(8)-C(8) ^{#3}	1.39(8)	S(7)–C(21)	1.75(3)
C(2)-C(2)#1	1.31(4)	C(18)-C(19)	1.38(3)

Table 2. Selected bond angles (deg) for 1. (Symmetry transformations used to generate equivalent atoms: $^{#1}x, -y, z$).

O(10)-W(1)-O(19)	160.0(7)	O(1)-W(1)-O(14)	102.9(7)
O(10)-W(1)-O(14)	87.7(8)	O(1)-W(1)-O(10)	99.9(8)
O(10)-W(1)-O(24)	85.0(7)	O(1)-W(1)-O(19)	100.1(6)
O(10)-W(1)-O(13)	87.8(8)	O(1)-W(1)-O(13)	97.0(7)
O(14)-W(1)-O(13)	160.1(5)	O(1)-W(1)-O(24)	170.8(7)
O(14)-W(1)-O(19)	88.9(6)	O(19)-W(1)-O(13)	88.7(6)
O(14)-W(1)-O(24)	85.0(5)	O(19)-W(1)-O(24)	75.1(5)
O(13)-W(1)-O(24)	75.3(5)	C(18)–S(4)–C(16)	96.4(11)
C(1)-S(2)-C(2)	96.8(10)	C(18)–S(5)–C(15)	96.2(12)
C(2)-S(1)-C(3)	95.6(11)	C(19)-S(6)-C(20)	93.4(14)
C(8)-S(3)-C(9)	97.8(17)	C(19)-S(7)-C(21)	94.5(13)
O(24)-B(1)-O(24) ^{#1}	110.0(17)	O(24)-B(1)-O(25)	111.3(12)
O(24) ^{#1} -B(1)-O(23)	108.4(12)	O(25)-B(1)-O(23)	107.4(17)

Owing to the stoichiometry of the salt, there must be four positive charges distributed among the seven DBTTF molecules, therefore giving rise to a mixedvalence state in the organic part. Previous work [20] has shown that it is possible to estimate the charge on each TTF molecule by looking at the central C=C and C-S bond lengths. An analysis of our structural data allows the degrees of ionicity for each type of DBTTF molecule to be estimated, although the relatively large

Table 3. Selected short contacts (Å) in 1.

$S(1) \cdots O(5)$	2.941	$S(5) \cdots O(2)$	3.282
$S(2) \cdots O(3)$	2.936	$S(5) \cdots O(14)$	3.281
S(3)····O(16)	3.112	$S(6) \cdots O(1)$	2.979
S(4)····O(12)	2.873	$S(7) \cdots O(20)$	3.096
$S(1) \cdots S(3)$	3.513	$S(4) \cdots S(7)$	3.299
$S(2) \cdots S(3)$	3.527	$S(5) \cdots S(6)$	3.416
$C(4A)-H(4A)\cdots O(5)$	2.654	$C(5A)-H(5A)\cdots O(22)$	2.442
$C(7A)-H(7A)\cdots O(3)$	2.506	$C(12A)-H(12A)\cdots O(17)$	2.430
$C(17A)-H(17A)\cdots O(12)$	2.458	C(24A)-H(24A)···O(8)	2.515
C(25)-H(25)···O(1)	2.594		



Fig. 3. Space-filling diagram of the 3D supramolecular network of $\mathbf{1}$ along the *b* axis, showing the 1D channels. H atoms of water molecules have been omitted for clarity.

standard deviations make this assignment not very secure. Thus, in molecule B, the C=C bond length is 1.39(8) Å, typical of a totally oxidized DBTTF radical cation. In molecule A, it is shorter (1.31(4) Å), typical for a neutral DBTTF molecule. In molecule C this distance is 1.38(3) Å, suggesting an intermediate degree of ionicity. Quite interestingly, this mixed-valence state has been confirmed by Raman spectroscopy (below).

The most unusual structural feature of **1** is that a 3D supramolecular network with 1D channels is formed (Fig. 3). The 1D channels are parallel to the *b* axis and possess dimensions of *ca*. 9.4×9.9 Å². The water molecules are filled in these channels. In the structure, two strong intermolecular contacts between the organic and the inorganic layers play an important role: one occurs between the sulfur atoms of the DBTTF molecules and the terminal as well as bridging oxygen atoms of the polyoxoanions with S…O distances as listed in Table 3. The second type is hydrogen bonding between oxygen atoms of the polyoxoanions and the ethylene group of the DBTTF molecules



Fig. 4. IR spectrum of **1**.



Fig. 5. Raman spectrum of 1.

with short C–H···O distances ranging from 2.430 (C12A–H12A···O17) to 2.654 Å (C4A–H4A···O5). These C–H···O hydrogen bonds and short S···O contacts make 1 an extended three-dimensional array. It is believed that the hydrogen bonding and π - π stacking interactions play a crucial role in assembling complicated supramolecular architectures.

Infrared, EPR and Raman spectroscopy

The IR spectrum of **1** contains several bands (Fig. 4). The A_g stretching modes of the central C=C bond (at 1340 and 1290 cm⁻¹) and one C–S–C internal mode (at 420 cm⁻¹) are observed. The appearance of two A_g ($\gamma_{C=C}$) central vibronic modes clearly reveals



Fig. 6. EPR spectrum of 1 at 298 K.

the presence of nonequivalent DBTTF molecules [21]. The peaks in the range of $400 - 1000 \text{ cm}^{-1}$ show the presence of a Keggin-heteropolyanion structure. The absorptions of the W–O_t bond in **1** (945 cm⁻¹) and in [(*n*-C₄H₉)₄N]₂H₃BW₁₂O₄₀ (950 cm⁻¹) [22] indicate that the anionic structure is unchanged, and that the interaction between the anions and the organic donor molecules is very weak.

In order to get precise information on the electron distribution in the organic substructure, we have performed Raman scattering measurements on **1**. There are at least four bands (Fig. 5) which can be readily assigned [23]: A totally symmetric stretching mode of the central C=C bond of DBTTF is observed at 1557 cm⁻¹ for neutral DBTTF; the stretching mode at 1414 cm⁻¹ corresponds to that of +1-ionized (ρ = +1) DBTTF molecules, and the band at 1470 cm⁻¹ indicates that another type of molecules is +3/4– ionized. Additionally, other Ag modes of DBTTF molecules are observed at 652 and 494 cm⁻¹.

At 298 K, the EPR spectrum of **1** displays a sharp Gauss-shaped signal at g = 2.04 (Fig. 6), which is close to g_e (2.0023) and attributable to the DBTTF⁺ radical cation. As there was no W⁵⁺ signal, it can be deduced that no reduced W atoms are present in **1**.

Experimental Section

Physical property measurements

The IR spectrum was recorded in the range $400-4000 \text{ cm}^{-1}$ on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. The EPR spectrum was recorded on a JES-FE3AX spectrometer at r.t. Raman spectra of powder

samples were recorded on a Lab Ram HR800 spectrophotometer. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. The W contents was determined by a Leaman inductively coupled plasma (ICP) spectrometer.

Electrocrystallization

The $[(n-C_4H_9)_4N]_2H_3BW_{12}O_{40} \cdot x H_2O$ salt and DBTTF were prepared according to literature procedures [22, 24]. Black single crystals of (DBTTF)₇[H₃BW₁₂O₄₀]₂·38H₂O were obtained by the electrochemical oxidation of DBTTF ($2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) in the presence of $[(n-C_4H_9)_4N]_2H_3BW_{12}O_{40}(4 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1})$ in an Ushaped cell with Pt electrodes separated by a sintered-glass frit. The crystallization took place after 6 days when using acetonitrile and 1,2-dichloroethane as solvents (1:1 v/v) and a low constant current of 0.6 μ A. The solvents were not previously dried, and it was necessary to add some drops of water to obtain good quality single crystals. – $C_{98}H_{138}B_2O_{118}S_{28}W_{24}$ (8533.51): calcd:

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C 13.78, H 1.62, W 51.70; found: C 13.65, H 1.73, W 51.53.

X-Ray data collection and structure determination

A black block crystal of (DBTTF)₇[H₃BW₁₂- $O_{40}]_2 \cdot 38H_2O$ with the approximate dimension $0.21 \times 0.20 \times 0.17 \text{ mm}^3$ was mounted on a glass capillary which was put on a Bruker Smart CCD diffractometer with Mo K_{α} radiation ($\lambda = 0.71073$ Å) at 293 K. 26411 reflections were measured, of which 9653 were unique $(R_{\text{int}} = 0.0847)$. An empirical absorption correction was applied. The structure was solved by Direct Methods and refined by full-matrix least squares on F^2 using the SHELX-97 software [25]. The non-hydrogen atoms were refined anisotropically. Monoclinic, space group C2/m; final R indices $[I \ge 2\sigma(I)]$: R1 = 0.0713, wR2 = 0.1622

CCDC 610961 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.

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