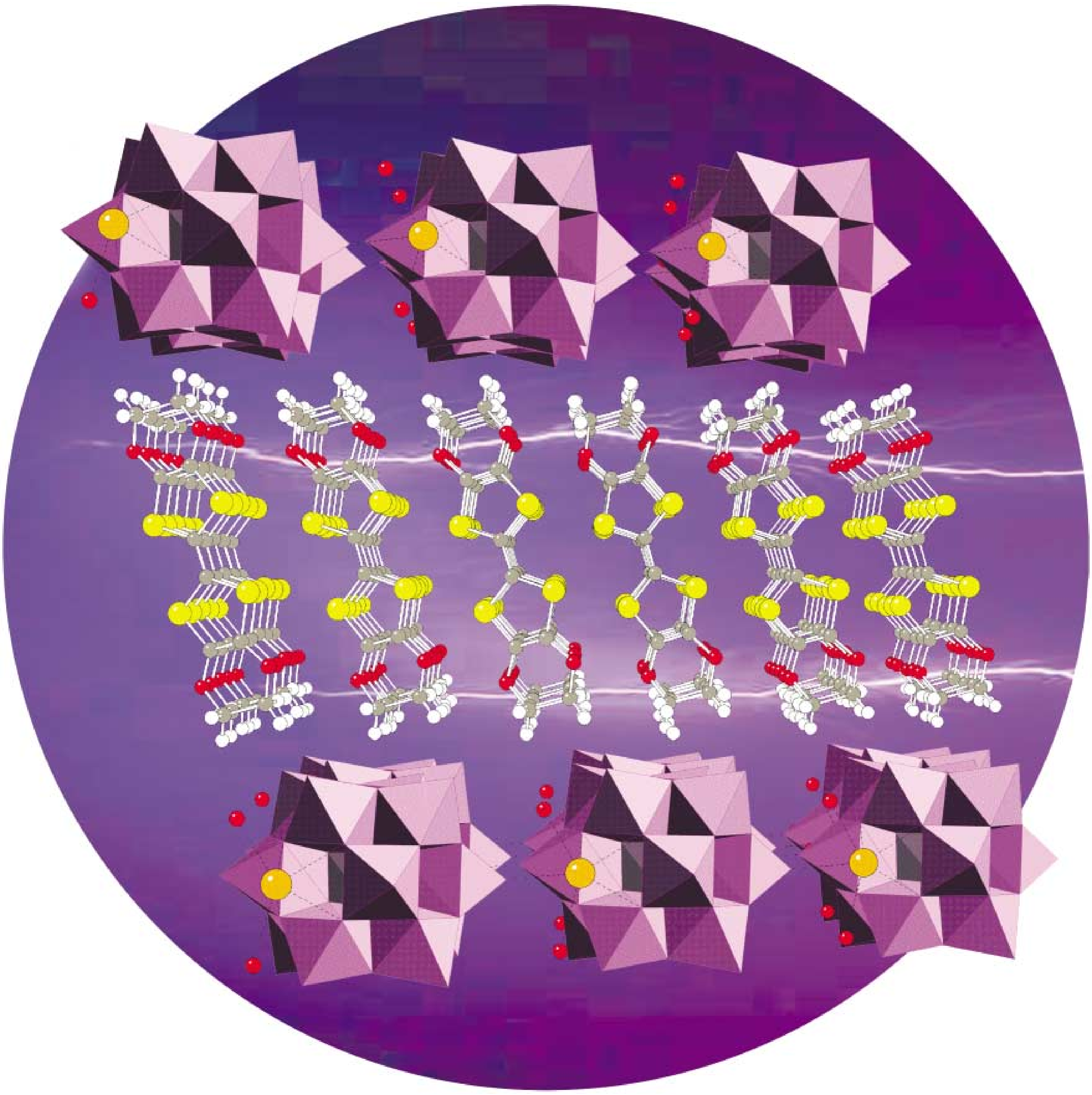
Zuschriften



Das erste Polyoxometallate enthaltende molekulare Material mit metallischen Eigenschaften besteht aus leitfähigen Schichten des Radikals Bis(ethylendioxo)tetrathiafulvalen, zwischen denen sich anorganische Schichten aus den Keggin-Polyoxometallaten $[BW_{12}O_{40}]^{5-}$ und K^+-Ionen befinden. Mehr dazu erfahren Sie in der Zuschrift von E. Coronado, C. Giménez-Saiz et al. auf den folgenden Seiten.

DOI: 10.1002/ange.200453985

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Conducting Materials

Metallic Conductivity Down to 2 K in a Polyoxometalate-Containing Radical Salt of BEDO-TTF**

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Owing to their structural and electronic versatilities polyoxometalate anions have proven to be useful inorganic components for the design of novel hybrid molecular materials with functional properties.[1] The application of these molecular metal-oxide clusters has been particularly pronounced in the field of molecular conductors. Typically molecular conductors are formed by segregated stacks of partially oxidized organic π-electron donor molecules of the tetrathiafulvalene (TTF) type interleaved by inorganic anions.[2] The use of polyoxometalates in this area has provided the opportunity to examine the strong structural effects produced by these highly charged and large anions on the organic packing. On the other hand, as a result of the ability of these anions to coordinate magnetic ions or to act as electron acceptors, they have afforded interesting hybrid materials either with coexistence of localized spins and delocalized electrons,[3] or with coexistence of delocalized electrons on both components.[4] However, the observation of metallic properties in this class of conducting materials has remained an elusive challenge. In fact, most of these radical salts are semiconductors or insulators, for example, the salts based on Keggin anions and TTF-type donors.[3–5]

In a few cases metallic-like properties have been observed but only at high temperatures. Two examples of this type are the series $[\mathrm{BEDT\text{-}TTF}]_{11}[\mathrm{P_2W_{17}MO_{62}}]$ ($\mathrm{M = W^{VI}, Re^{VI}}$)[6] and the compound $[\mathrm{BEDT\text{-}TTF}]_5[\mathrm{VW_5O_{19}}]\cdot 6\,\mathrm{H_2O}$,[7] which exhibit metallic behavior down to 240–260 K with room temperature conductivities between 10–14 S cm^{-1}. Below these temperatures broad metal-to-semiconductor transitions are observed. A significant improvement has been obtained in the compounds $[\mathrm{BEDT\text{-}TTF}]_5[\mathrm{H_3V_{10}O_{28}}]\cdot 4\,\mathrm{H_2O}$[8] and $[\mathrm{BEDT\text{-}TTF}]_6[\mathrm{Mo_8O_{26}}]\cdot(\mathrm{DMF})_3$[9] which behave as metals down to 50 and 60 K with room temperature conductivities of 360 and 3 S cm^{-1}, respectively.

Herein we report the first example of a polyoxometalate-based radical salt that exhibits metallic behavior down to 2 K. The compound, formulated as $[\mathrm{BEDO\text{-}TTF}]_6\mathrm{K_2}[\mathrm{BW_{12}O_{40}}]\cdot 11\,\mathrm{H_2O}$ (**1**), is formed by the polyoxometalate ion $[\mathrm{BW_{12}O_{40}}]^{5-}$ and the organic radical bis(ethylenedioxo)tetrathiafulvalene (BEDO-TTF). To our knowledge, in spite of its potential interest, no polyoxometalate-containing radical salt with the donor BEDO-TTF has been reported to date. Most radical salts containing the BEDO-TTF donor are molecular metals, including the superconductors, $[\mathrm{BEDO\text{-}TTF}]_3[\mathrm{Cu_2(NCS)_3}]$[10] and $[\mathrm{BEDO\text{-}TTF}]_2[\mathrm{ReO_4}]\cdot\mathrm{H_2O}$.[11] Moreover, as an oxygenated donor BEDO-TTF could establish stronger intermolecular interactions (of the type O···O) with the metal-oxide clusters than other donors which do not contain oxygen, such as bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF).

For these reasons, we have made numerous attempts to obtain radical salts containing the BEDO-TTF donor and Keggin polyoxometalates. However, whereas the donor BEDT-TTF has given rise to extensive series of crystalline radical salts with many different polyoxoanions possessing the Keggin structure, the synthesis of analogue salts based on BEDO-TTF has turned out to be much more difficult. In fact, the use of $[\mathrm{R_4N}]^+$ acid salts of Keggin polyoxometalates as starting salts has not given any positive results, however, mixed $[\mathrm{R_4N}]^+$ and $\mathrm{K^+}$ salts afforded small single crystals of compound **1**. It seems that the $\mathrm{K^+}$ ions, which enter into the structure, play an important role in stabilizing the salt and furthermore, they reduce the effective charge of the polyoxoanion and therefore the charge of the BEDO-TTF molecules.

The electrocrystallization method produced single crystals of compound **1** which were too weakly diffracting to perform a X-ray data collection on diffractometers equipped with conventional X-ray sources, but a reasonable diffraction pattern could be obtained using the high intensity of the synchrotron radiation produced at the Swiss-Norwegian Beamline at the European Synchrotron Radiation Facility in Grenoble (France). The structure of this radical salt[12] consists of alternating layers of organic donors and inorganic polyoxometalates in the [$\tfrac{1}{2}$, $\tfrac{1}{4}$, 1] direction (Figure 1).

The organic layers are made up of three crystallographically independent BEDO-TTF units (labeled as A, B, and C in Figure 2) which arrange forming very uniform stacks parallel to the *b* axis, following the sequence …ABC… in one chain and the opposite one (…CBA…) in the adjacent chains (Figure 2).

The organic layers adopt the so-called β″ packing arrangement[13] with stacks of BEDO-TTF molecules having numerous short intermolecular S···S and S···O separations which are shorter than the sum of the van der Waals radii (3.60 Å and 3.32 Å respectively, see Supporting Information).

Despite being crystallographically independent the three organic donors (A–C) all have the same geometry: they all have the same twisted, eclipsed conformation of their outer

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[**] This work was supported from the Spanish Ministry of Science and Technology, MCyT (MAT2001-3501-C02-01). CGS thanks the MCyT for a research contract (Programa Ramón y Cajal). We thank the SNBL and the ESRF for allocation of beam time (proposal CH-897). BEDO-TTF = bis(ethylenedioxo)tetrathiafulvalene.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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DOI: 10.1002/ange.200453985

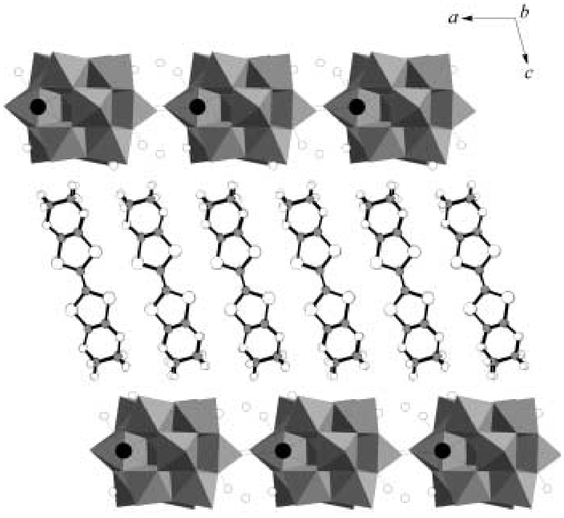

Figure 1. Structure of **1** showing the alternating layers of the polyoxoanions and the organic donors.

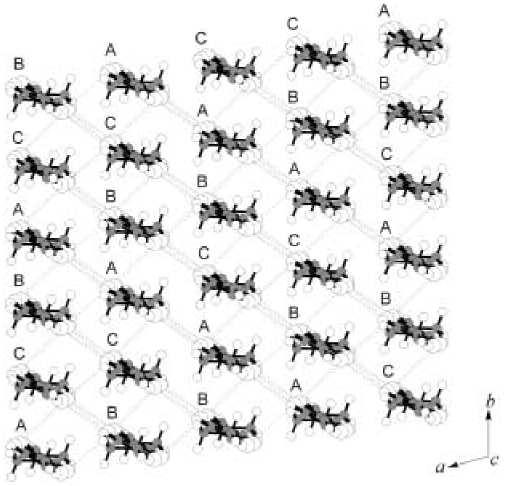

Figure 2. View of the organic layer showing the labeling of the three crystallographically independent BEDO-TTF molecules. Dotted lines represent S···S and S···O contacts shorter that the sum of the van der Waals radii.

ethylene groups, as well as similar intramolecular bond lengths and angles. This is a noteworthy difference with respect to the other radical salts of Keggin polyoxometalates with the related donors BEDT-TTF[3] and BEDSe-TTF (bis(ethylenediselena)tetrathiafulvalene),[4] in which the organic molecules have very different conformations, geometries, and charges, and form very irregular and exotic stacks or even lose the typical 2D packings that these donors usually form when they are combined with simpler anions. This general feature of the polyoxometalate-containing radical salts has been attributed to the large charges and volumes of these anions and ultimately leads to charge localization and thus, to poor conducting properties.[2]

In the present case the formation of very uniform organic stacks seems to be a result of the use of the oxygenated donor BEDO-TTF, which gives rise to many short intermolecular C–H···O contacts that stabilize the formation of the eclipsed stacks characteristic of the β″ packing (typical for most BEDO-TTF-based organic metals). Figure 3 shows one stack of donor molecules in which the dotted lines represent intrastack C–H···O contacts shorter than the sum of the van der Waals radii (2.72 Å). The hydrogen atoms of the donors that do not establish short intrastack contacts with other donors, form C–H···O contacts with the oxygen atoms of the polyoxoanion or the water molecules, these C–H···O separations are between 2.37 and 2.94 Å.

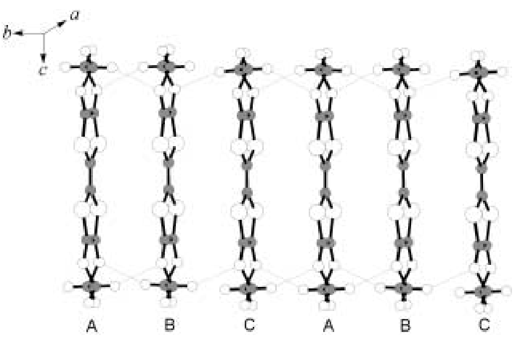

Figure 3. View of one eclipsed stack of organic donors. Dotted lines represent C–H···O contacts shorter than 2.72 Å (the sum of the van der Waals radii); A–C as in Figure 2.

The inorganic layers are formed by the bulky Keggin polyoxometalates and the K^+ ions inserted between them. There is only one kind of K^+ ion, it has a coordination number of 8 (K···O, 2.69–2.98 Å) and is coordinated to oxygen centers of three different polyoxoanions as well as two water molecules of crystallization which do not have short contacts with the ethylene groups of the organic donors.

The K^+ ions inserted in the inorganic layers fill the cavities or voids existing in between the Keggin polyoxometalates. In the other Keggin-based radical salts the organic donors fill these voids by "docking" of the outer ethylene groups into the cavities provided by the polyoxometalate network. This feature often yields irregular stacks of the donors.[2] In compound **1** the insertion of K^+ ions is related to the formation of fully eclipsed stacks of BEDO-TTF units which can not fill the cavities created in the inorganic sublattice.

The analysis of the bond lengths of the three independent BEDO-TTF molecules suggest that they are partially oxidized with a charge of $+0.5$, in agreement with the anionic charge and the stoichiometry of the salt.[14]

The thermal variation of the electrical conductivity (σ) of **1** along the best developed face of a single crystal is shown in Figure 4. The room temperature conductivity is about $37\,\mathrm{S\,cm^{-1}}$ and gradually increases as the temperature is decreased to reach a maximum value of $910\,\mathrm{S\,cm^{-1}}$ at 2 K. This behavior reveals a metallic character of this salt across the studied temperature range (300–2 K). The temperature dependence of the resistivity ($\rho = 1/\sigma$) shows a linear dependence from room temperature to 200 K, which is usually associated with electron–phonon scattering.[9] Below this temperature the resistivity is proportional to T^2 (inset in

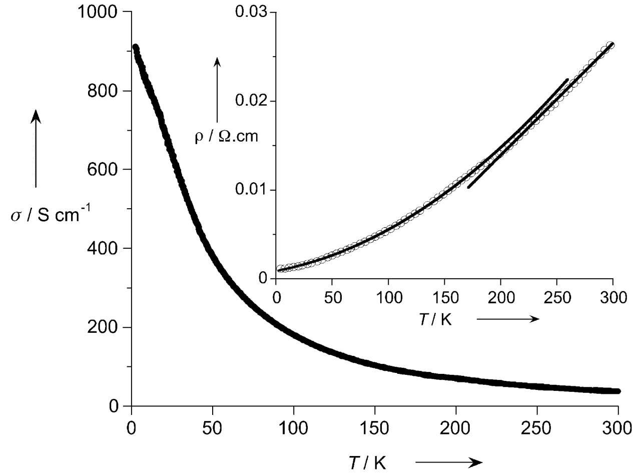

Figure 4. Thermal variation of the conductivity (σ) of **1** showing the metallic behavior down to 2 K. Inset: Plot of the thermal variation of the resistivity (ρ). Solid lines show the linear and quadratic dependencies of ρ above and below 200 K, respectively.

Figure 4), typical of metallic organic salts where electron–electron scattering is the dominant mechanism of conductivity.[9]

The thermal variation of the molar magnetic susceptibility, χ_m, of **1** (not shown) has an almost constant value of 0.013 emu mol^{-1} from room temperature to approximately 15 K. Below this temperature χ_m shows a continuous increase reaching a value of around 0.021 emu mol^{-1} at 2 K. This behavior can be accurately reproduced with a simple model considering a Curie tail (C/T) with $C = 0.017$ emu K mol^{-1} plus a temperature-independent paramagnetism corresponding to the so-called Pauli paramagnetism of 0.013 emu mol^{-1}. This value is similar to those obtained in other synthetic metals and confirms the metallic character of this salt. The low C value indicates the presence of a very small paramagnetic impurity, already observed in many other radical salts and attributed to the presence of isolated donor molecules as the result of the ubiquitous crystal defects (less than 0.8 % of isolated BEDO–TTF$^+$ radicals). The room temperature ESR spectrum of **1** (not shown) has a single line centered at $g = 2.0059$ with a line width of 40 G, typical of this kind of radical salts.[2] The high value of the line width suggests a marked 2D electronic character in **1**, as indicated by the electrical properties.

In conclusion, the organic/inorganic hybrid material presented herein is the first example of a polyoxometalate-containing radical salt that exhibits a metallic behavior down to 2 K. This result demonstrates that it is possible to use bulky and highly charged polyoxoanions as components of new radical salts that behave as a metal and opens up the possibility of synthesizing new molecular materials with coexisting or even coupling of conducting electrons and localized magnetic moments. The synthetic strategy simply consists in combining the BEDO-TTF donor with inorganic layers of magnetic Keggin polyoxometalates and K$^+$ ions. This would give rise to a new series of molecular materials, similar to the reported series with the BEDT-TTF donor,[3] but with the advantage of having a metallic behavior down to very low temperatures.

Experimental Section

Crystals of compound **1** were prepared by electrocrystallization of a 3:2 mixture of 1,1,2-trichloroethane/acetonitrile containing the soluble salt $(n\mathrm{Bu}_4\mathrm{N})_4\mathrm{K}[\mathrm{BW}_{12}\mathrm{O}_{40}]$ (10^{-2} M), the organic donor BEDO-TTF (2×10^{-3} M), and some drops of distilled water. The donor was slowly oxidized at a constant current of 1.2 μA. Under these conditions very thin, plate-like, brown single crystals were obtained on the platinum electrode of the electrochemical cell after 7 days. When dry conditions were used, no crystal growth was detected on the electrode after 20 days, indicating that water molecules are required for the stabilization of the crystal structure.

D.C. conductivity measurements over the range 2–300 K were performed using the four contacts method in several different single crystals, all the samples gave reproducible results. Contacts between the crystals and platinum wires (25 μm diameter) were made using graphite paste. The samples were measured in a Quantum Design PPMS-9 with a dc current of 1 μA. The cooling and warming rate was 1 K min^{-1} and the results were, within experimental error, identical in the cooling and warming sweeps.

Variable temperature susceptibility measurements were carried out in the temperature range 2–300 K at a magnetic field of 0.1 T on a polycrystalline sample with a magnetometer (Quantum Design MPMS-XL-5) equipped with a SQUID (superconducting quantum interference device) sensor. The susceptibility data were corrected for the diamagnetic contributions as deduced by using Pascal's constant tables and for the sample holder. The room temperature ESR spectrum of the same polycrystalline sample was recorded at X-band with a Bruker E500 spectrometer.

Received: February 10, 2004 [Z53985]

Keywords: conducting materials · crystal engineering · hybrid materials · polyoxometalates

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[12] Crystallography: Intensity data were collected at the Swiss-Norwegian Beamlines at ESRF, at 120(2) K on a minute crystal of **1** (size 0.10 × 0.02 × 0.02 mm) using synchrotron radiation ($\lambda = 0.6804(2)$ Å). The 345 mm diameter of a MAR345 image plate was used with a pixel size of 0.15 mm. A full rotation around the spindle axis of the MAR345 was performed, with a rotation width of 2°; the sample to detector distance was set to 100 mm for a resolution at the edge of the image plate of 0.74 Å ($2\theta_{max} = 54.70°$). Diffuse scattering was observed in the data (see Supporting Information) but no corrections to the Bragg intensities were made. The 179 images collected were processed using the program CrysAlisRED (Oxford Diffraction Ldt., CrysAlis Software System, Version 1.169.9, Oxford, England, **2002**) to obtain the average crystal structure. Cell dimensions and space group were determined from 4372 very intense reflections selected throughout the data collection. A total of 60103 reflections have been integrated, 13463 of which unique ($R_{int} = 0.0753$), for a final completeness of the dataset of 98%. The structure was solved by direct methods and refined by full matrix least-squares on F^2 using SHELX97 (G. M. Sheldrick, SHELX-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1998**). Six independent water molecules were found, one of them having a refined occupancy of 0.5. All non-hydrogen atoms were refined anisotropically with the exception of six atoms of the polyoxoanion, one carbon atom of the organic donor, and the water molecules. Hydrogen atoms on carbon atoms were included at calculated positions and refined with a riding model. Crystal data for **1**: $C_{60}H_{70}B_1O_{75}S_{24}W_{12}K_2$, $M_r = 5055.81$, triclinic, space group $P\bar{1}$, $T = 120(2)$ K, $a = 11.728(2)$, $b = 11.948(2)$, $c = 23.335(5)$ Å, $\alpha = 90.13(3)°$, $\beta = 102.20(3)°$, $\gamma = 117.43(3)°$, $V = 2817.9(9)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.979$ Mg m^{-3}, $\mu = 12.82$ mm^{-1}, $F(000) = 2345$, 13463 unique reflections, 738 parameters, 29 restraints, final agreement factors (all data): $R1 = 0.0940$, $wR2 = 0.2313$, GOF = 1.152. CCDC 230883 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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